

Glycerol for renewable acrolein production by catalytic dehydration



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ABSTRACT

The significant surge in biodiesel production by transesterification of edible or non-edible oils have caused surplus of glycerol in the market. With its characteristics, unique structure, renewability, and bio-availability, glycerol has tremendous potential to be transformed to higher value-added chemicals. This article provides a comprehensive and critical review of glycerol dehydration to acrolein in both petroleum-and bio-based processes. Acrolein has enormous industrial applications as a significant chemical intermediate for acrylic acid, DL-Methionine and superabsorbent polymer production. The current development of several precursors on suitable support such as heteropoly acids, zeolites, mixed metal oxides, and pyrophosphates in creating superior catalytic properties for both liquid- and gas-phase processes has been discussed. The acidity and textural properties of various catalysts, as significant variables affecting acrolein yield and selectivity, are evaluated separately. Techno-economical evaluation on dehydration of petroleum- and bio-based glycerol to acrolein proved that the bio-based processes are more feasible compared to the conventional petroleum-based process. In addition, various proposed mechanisms for catalytic dehydration of glycerol to acrolein have been examined. Particularly, catalyst coking and few crude glycerol applications have been identified as the main drawbacks for immediate industrialization and commercialization of glycerol dehydration to acrolein.

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1. Introduction

In the early 20th century, the majority of bulk chemicals were produced based on biotechnology such as fermentation of potatoes and corn. However, the successful cracking of petroleum to simpler hydrocarbons was the breakthrough for new type of chemistry and chemical productions. Chemicals are an integral factor of our daily life today. It means all sectors of humans' life rely on chemicals which inevitably enhanced the production of various types of chemicals daily. It is reported that the global chemicals output reached to US\$ 4.12 trillion by 2010 [1].

Relentless environmental concerns, steep hike in fossil fuel price, and increasing demand of non-renewable fossil fuels consumption have dramatically increased global search for alternative energy, particularly biodiesel [2–4]. Indeed, biodiesel decreases engine emissions such as sulfur oxides (100%), un-burned hydrocarbons (68%), and polycyclic aromatic hydrocarbons (80–90%), significantly [5–6]. Biodiesel is environmental friendly, technically feasible, and biodegradable [7]. Various plant lipids and animal fats are suitable sources for biodiesel production. For economical purposes, many researchers have recently focused on non-edible or waste oils to decrease the production costs by 60–90% [8].

Many parts of the world have devised plans to enhance their biodiesel production [9]. Europe and USA, for instance, produced 7.8 and 2.3 million ton of biodiesel in 2008, respectively and planned to double production by 2012 [10]. In addition, it is estimated that the global biodiesel market will dramatically increase to 37 billion gal by 2016 [11]. Generally, 1 mol of glycerol is formed for every 3 mol of biodiesel production. On the other hand, 10 wt% of the total transesterification process production is glycerol [12–13]. In accordance with the worldwide surge in biodiesel production, over 1.54 million ton of glycerol is anticipated in 2015 [10]. The huge amount of biodiesel production worldwide largely affects the glycerol price.

1.1. Glycerol

Glycerol will become the major chemical for future bio-refineries. According to recent studies, glycerol was detected as one of the top 12 most important bio-based chemicals in the world [14]. Many researchers have demonstrated that glycerol, as the by product can decrease biodiesel (B100) production costs by half from 0.63 to 0.35US\$ per liter [15–16]. Nevertheless, glycerol can be produced through different processes such as (1) fatty acid production, (2) microbial fermentation, (3) soap manufacture, (4) biodiesel production, and (5) propylene oxide synthesize. Meanwhile, glycerol can be produced by the fermentation of sugars (glucose and fructose) and industrial conversion of lignocelluloses into ethanol [17–19].

Glycerol purity is the key factor for its industrial application. Traditionally, industrial biodiesel plants used homogeneous acids (H_2SO_4 , HCl) and alkali (NaOH, KOH) catalysts. Thus, glycerol produced by conventional processes includes other products such as methanol, water, residual catalyst, free fatty acids, un-reacted mono-, di-, and tri-glycerides, methyl ester and various organic and inorganic compounds (matter organic non-glycerol (MONG)) [20–21]. Thus, low quality glycerol requires treatment, which includes neutralization by phosphoric acid (H_3PO_4) or recycling in order to eliminate excess methanol, catalyst and soap. In

addition, residual methanol can be omitted by evaporation after acidulation and separation of FFAs although residual methanol content can create hazardous wastes. The final glycerol with approximately 80–95% purity will be sold to the industrial refineries at low cost [14–15]. However, the purification processes are costly and uneconomical. Hence, some industries prefer to burn the low quality glycerol as waste material and use pure (> 98.5%) glycerol instead of purified crude glycerol. As a result, more than 150,000 and 250,000 metric tons of crude glycerol was tragically burnt in 2006 and 2007, respectively, wasting one of the most valuable organic raw material [22–23].

The current trend sees majority of researchers focused on heterogeneous catalyst application for biodiesel production for higher quality biodiesel and glycerol production. Bourney et al. [24] investigated the biodiesel production in a continuous process by zinc and aluminum (Zn-Al) mixed oxides as heterogeneous solid catalyst. They reported 98.3% and 98% purity for the final biodiesel and glycerol products, respectively. As a result, their catalytic process could eliminate all costly treatment and purification processes for the direct applications of the produced glycerol to industries such as pharmaceutical, cosmetics and food [24]. The industrial glycerol utilization for value-added chemicals attracted much attention, not only due to the surplus of glycerol available, but also because glycerol is edible, bio-sustainable, non-toxic, and biodegradable. The multi-functional structure and physico-chemical characteristics of glycerol lead to various applications of glycerol in different reaction pathways [21,24–28].

The three most important value-added chemicals that can be produced from glycerol are 1,3-propanediol, hydrogen, and acrolein. The wide application of 1,3-propanediol in production of polymers, foods, medicines, cosmetics, and lubricants [29] demonstrated that the production rate of this material is limited because of high production costs. Therefore, utilization of glycerol as a renewable feedstock significantly decreases the 1,3-propanediol production cost since the glycerol price is less than fossil fuels. Besides, glycerol is abundantly available [30]. Fermentation, hydrogenolysis, and dehydroxylation are different reactions for production of 1,3-propanediol from glycerol. The fermentation processes perform in two-step enzymatic reactions. Glycerol changes to 3-hydroxypropionaldehyde (3-HPA) and water in the first step and then 3-HPA is reduced to 1,3-propanediol [31].

Hydrogen is another value-added chemical that can be produced from glycerol by auto-thermal reforming, steam reforming, and partial oxidation [32]. The steam reforming process is performed in three steps: glycerol dehydrogenation (CO bonded on to the catalyst surface), desorption, and finally water-gas shift or methanation [29] to react glycerol with water for hydrogen production. Furthermore, a substrate reacts with oxygen at sub-stoichiometric ratios in the partial oxidation process. Moreover, the auto-thermal reforming method mixes the effect of steam reforming and partial oxidation by feeding the mixture of air, water, and fuel to the reactor [32].

The third main chemical that can be produced from glycerol is acrolein that will be deliberately discussed in this review. Acrolein is also known as 2-propenal or acrylic aldehyde which is the simplest unsaturated aldehyde [32]. Acrolein is produced by dehydration of glycerol in the presence of catalyst.

Low cost glycerol is attractive for commercialization application (more than 2000) to polymers, ethers, and other valuable

materials [33]. Glycerol is insoluble in hydrocarbon, but, completely soluble in alcohols and water due to its three hydroxyl groups [34]. By controlling its water content, glycerol can change to a very hydrophilic compound, and be easily used in glue or other adhesives. In addition, the three hydroxyl groups cause high viscosity and boiling point (563 K) for glycerol due to the formation of inter- and intra-molecular hydrogen networks. Therefore, glycerol can be utilized in resins and plastics as a softener and also for pharmaceutical applications as a lubricant due to its rheological characteristic. Furthermore, the non-toxic glycerol can be used in food, medicines, and cosmetic materials since it has sweet taste [35].

The wide applications of glycerol in our daily life are illustrated in Fig. 1. Glycerol is being used in moisturizers, sweeteners or food and drink preservatives. Since glycerol has a non-toxic nature it is also widely used in cosmetics and toiletries. Moreover, glycerol is also utilized in paper and printing industry for softening and reducing shrinkage during paper manufacturing. In tobacco industry, glycerol is being used to prevent breaking and crumbling during cigarette processing while it also adds flavor to tobacco.

There are two possible categories for glycerol industrial (large scale) application. The first is the utilization of glycerol for obtaining fine chemicals such as hydrochlorination of glycerol for chlorohydrins, an important intermediate for epichlorohydrin production. Fig. 2a illustrates the related reaction steps. This reaction is selective to produce 1,3-dichlorohydrin. The product is a mixture of 1,3- and 1,2-dichlorohydrin (70–30%). Adding glycerol is the main advantage

to this process since 1,3-dichlorohydrin is more reactive than 1,2-dichlorohydrin. Fig. 2b indicates the two-step reactions for dehydration of glycerol to acrolein followed by oxidation for acrylic acid production. The conventional process for acrylic acid production is a two-step propene oxidation with different catalysts. However, in the new approach, glycerol, instead of propene is utilized, which is more economical compared to the petroleum-based conventional methods.

The other category is the production of oxygenated additives for fuels from glycerol such as esters (triacetin) [37], ethers (glycerol isobutylethers) [38–40], ketals [41], and acetals [41–42]. The etherification of glycerol for production of a mixture of di- and tri-butyl ethers of glycerin (h-GTBE) is the most promising reaction since it is a new additive for gasoline and h-GTBE improves the octane and decreases the pour and cloud point and also diesel viscosity. Fig. 3 summarizes several materials that can be produced from glycerol by various processes. Other glycerol industrial applications include

- (1) halogenations to epichlorohydrin, which is a significant intermediate for epoxy resins (commercialized by Solvay in France at 2007);
- (2) syngas production in the presence of Pt-Rh catalyst. In addition, alkanes and methanol production by Fischer Tropsch process (industrialized by BioMCN with 200 kJ/yr capacity Netherland) [43–44];

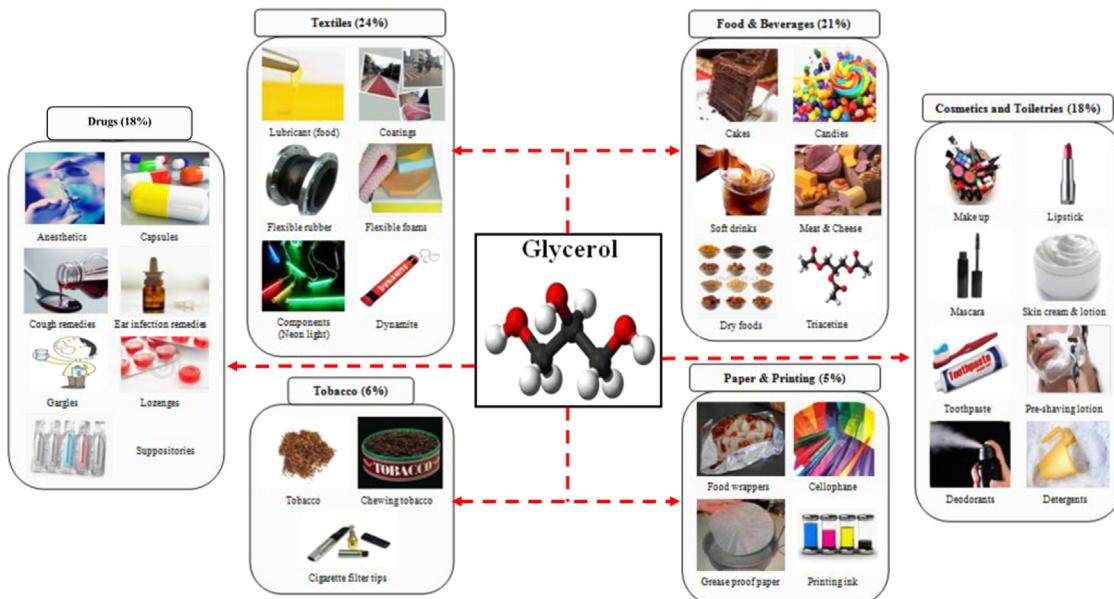


Fig. 1. Glycerol distribution by application.

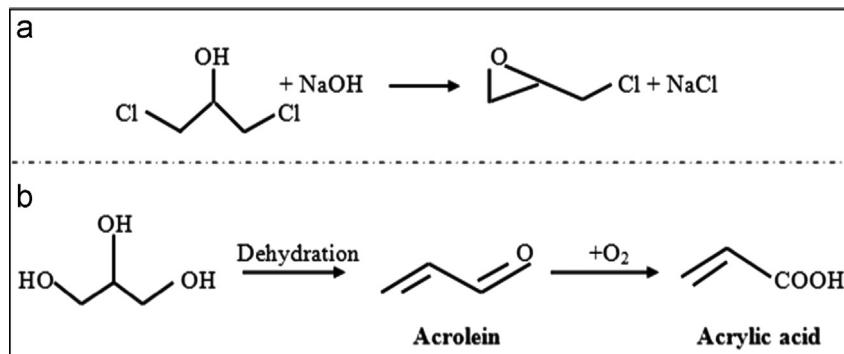


Fig. 2. (a) Hydrochlorination of glycerol for chlorohydrins production and (b) two step reaction of acrolein and acrylic acid production [36].

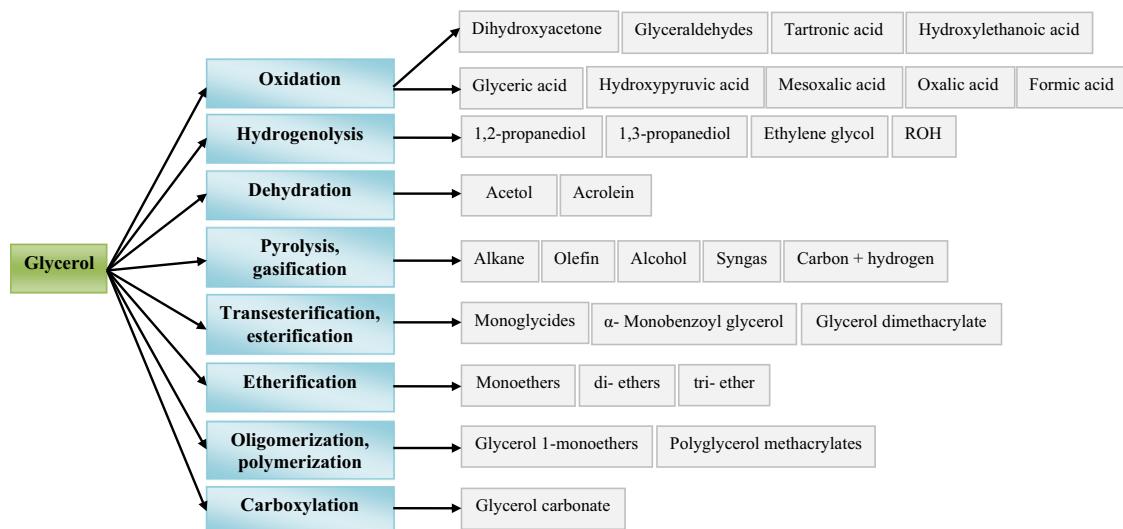


Fig. 3. Glycerol conversion methods for different value-added chemical production.

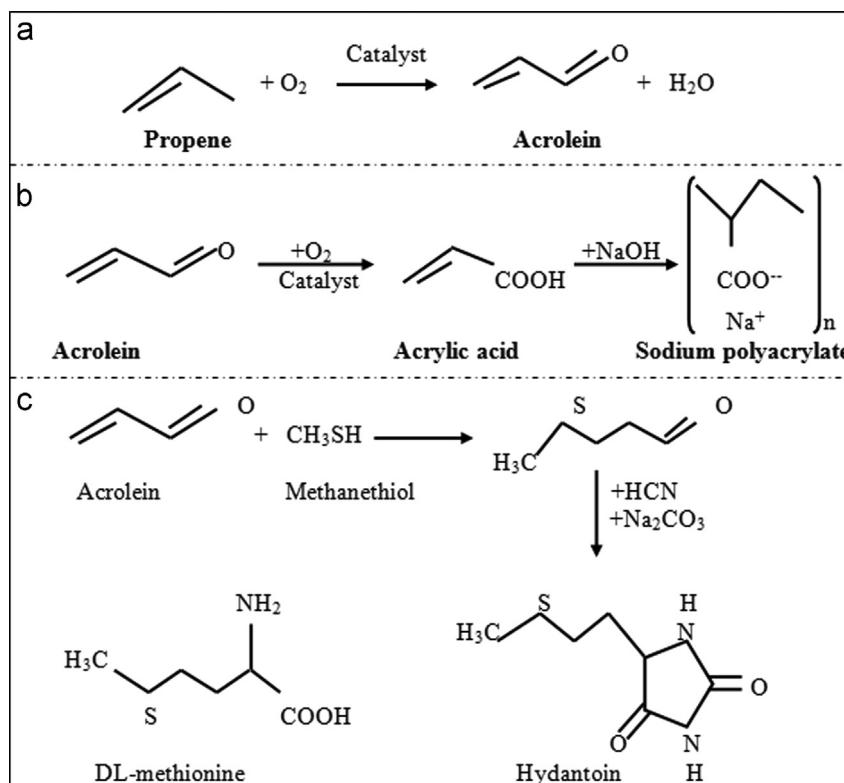


Fig. 4. (a) The conventional industrial process for acrolein production [47], (b) the reaction steps for sodium polyacrylate production, and (c) the reaction pathways for DL-Methionine production from 3-methylthio-propionaldehyde [10].

- (3) production of monoacylglycerol (MAG) and diacylglycerol (DAG) as emulsifiers in cosmetic and food (sauce and margarines) industries by esterification of glycerol [45];
- (4) selective reduction of glycerol to propylene glycol (MPG) or 1,3-propanediol (PD) (Syngas Chemicals commercialized MPG production by 30 kJ/year capacity) [46].

1.2. Acrolein

The conventional method for acrolein production is propene selective oxidation in the presence of complex BiMoO_x based catalyst (Fig. 4a) with approximately 85% acrolein selectivity at

95% propene conversion [47]. However, petrochemical exhaustion is foreseen in the near future. Therefore, the production of more important industrial materials such as acrolein from sustainable and renewable resource is prevalent recently. The main obstacle for such an industrial (large scale) application is economical matters. According to recent reports, the production of acrolein from glycerol can be commercialized if the glycerol price becomes less than 300US\$/ton [48]. The controlling factor is the application of low cost crude glycerol that was only 100US\$/t in 2010 in contrast with refined glycerol that was 500–550US\$/t in the same year. Bourne et al. [24] introduced a new application of heterogeneous catalyst in industrial biodiesel production plant. They produced high quality (> 98%) glycerol as a by-product of

biodiesel that significantly decreased the downstream purification and refinery costs of crude glycerol. The quality of the product made it a competitive feed stock for large scale applications.

Acrolein is highly toxic; therefore, it should be directly converted into other value-added chemicals such as acrylic acid, which is used to produce sodium polyacrylate (Fig. 4b). The polyacrylate is a superabsorbent polymer (SAP) used in hygiene products such as diapers. This material can extremely absorb liquids (more than 500 times of its weight) [49]. In 2010, it was estimated that SAP has an annual market of 1.9 million tons. The other acrolein application is in DL-Methionine production from 3-methylthio-propionaldehyde as the intermediate (Fig. 4c). The DL-Methionine improves animal growth and so it is widely used in meat production. In addition, DL-Methionine is a very important amino-acid that cannot be produced by living organisms. Due to its low production (only 500 kt/yr), large scale synthesis is desirable since the worldwide meat consumption will increase by 3–7% in the near future [50]. Methionine deficiency in nutrition can lead to various types of disease and physiological conditions such as muscle paralysis, depression, childhood rheumatic fever, schizophrenia, toxemia, hair loss, Parkinson's liver deterioration, and impaired growth [51]. Fig. 5 illustrates all possible chemicals that can be produced from acrolein. 1,3-Propanediol has important applications such as transparent ballistic polymer. The polymer is a life-saving technology for the war fighters, and it also used in impact-resistant eyeglass lenses. Polytrimethylene terephthalate (PTT) is another valuable material that can be produced from acrolein. The PTT is widely using in carpet and textile manufacturing.

The main objective of this review is to provide a comprehensive documentation on acrolein production by both liquid- and gas-phase dehydration. In addition, the influence of physico-chemical catalyst characteristics such as acidity and textural properties on this process is presented. Furthermore, the application of crude glycerol as a low-cost feed stock for acrolein production as well as techno-economical evaluation of bio-based and petroleum-based acrolein production are also reported. This review should contribute towards increasing more researches related to acrolein production by dehydration of glycerol and possibly hasten the approach towards the commercialization of this process.

2. Petroleum-based acrolein production

The production of acrolein was an important issue at the beginning of the 20th century and many researchers attempted to propose better industrial approach for acrolein production during the last decades. The first industrial process was invented by Degussa in 1942. They produced acrolein by aldol condensation of formaldehyde and acetaldehyde [52]. This method had some disadvantages such as incomplete conversion of raw material that led to separation problems in the downstream. The second process that emerged at the end of the 1950s was partial oxidation of propylene. This process became a very interesting method at that time due to availability of cheap propylene. The Shell Company initiated the gas-phase acrolein production by partial oxidation of propylene in 1958 followed by stand oil of Ohio (SOHIO) which identified bismuth molybdate as the catalyst for an economical and high yield acrolein production. The partial oxidation of propylene remained the main process for acrolein production till now. Other feedstocks such as propane, a byproduct of oil refining and natural gas production processes, attracted a lot of attention due to its lower costs [53]. However, there is no report for commercial viability of acrolein production by partial oxidation of propane probably due to low acrolein yield.

The other possible processes for acrolein production includes utilization of nickel phosphate or silica-supported metal oxides (tungsten, zinc, nickel, and magnesium) with formaldehyde and ethanol [54], oxidation of allyl alcohol [55–56], decomposition of allyl ether [57], and partial oxidation of ethane [58]. However, low availability of raw materials, expensive reactant, high energy demand, low selectivity, and difficult application in a large scale plant hindered the commercialization of these processes. Fig. 6 illustrates all possible acrolein synthesis methods.

2.1. Partial oxidation of propylene to acrolein

The main conventional process for industrial production of acrolein is partial oxidation of propylene as shown below

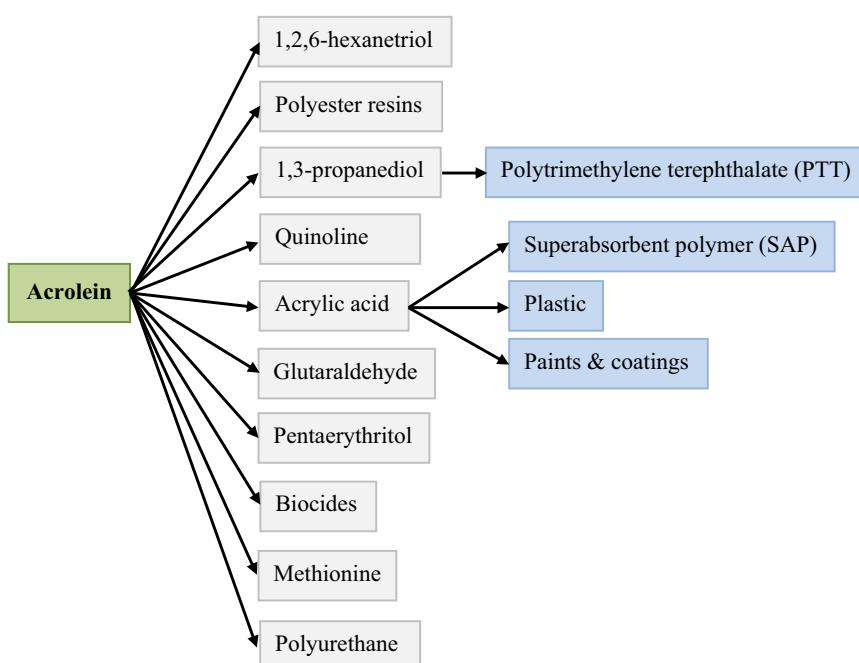
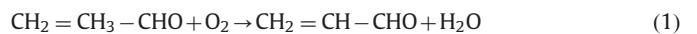


Fig. 5. Possible chemicals that can be produced from acrolein.

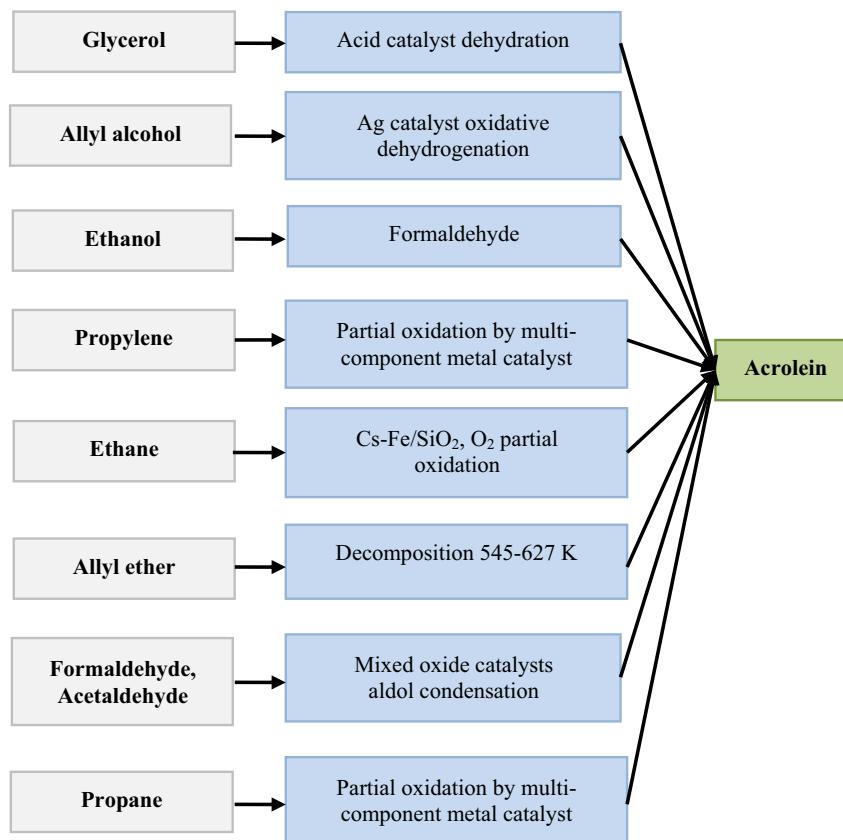


Fig. 6. Various synthesis methods for acrolein production.

Generally, the partial oxidation of propylene occurred in a multi-tubular reactor consisting of tubes at 523–673 K in the presence of multi-component catalysts [59]. The Mo–Bi–X"–X"(–X'–Y–Z)–O is a general formula of multi-component metal catalyst. The Mo–Bi–X"–X" section is the basic structure with four necessary metal components such as Ni, Co, Mg, Ne, Pb, Cr, Fe, Ce, Al and bismuth molybdate which act as the main active sites that are located on the surface of catalyst particles. However, the highest catalytic activity was reported in the presence of both divalent (Co^{2+}) and trivalent (Fe^{3+}) metal compounds. In addition, the (–X'–Y–Z)–O component includes the alkaline metals (X'), Sb, Te, W, V, or Nb (Y), and P or B (Z). The acrolein production was improved by steam co-feeding with the reactant gas [60,61]. More importantly, the service life of these catalysts was around 2–5 years. Table 1 presents various researches in petroleum-based acrolein production.

The gas-phase partial oxidation of propylene to acrolein is highly exothermic. Thus, some researchers attempted to improve this process by designing a reactor to efficiently release the heat during the reaction. The proposed approaches are summarized in Table 2.

Fig. 7 illustrates the reaction mechanism for partial oxidation of propylene to acrolein. The reaction started with formation of Mo-bound allyl intermediate by coordination of C=C double bond of propylene and the Bi–Mo site of catalyst. According to the application of different catalysts the rate-determining step happened at the bridging O atom (Fig. 7a) or at the carbonyl site of Bi atom (Fig. 7b) [88–90]. Later, the O insertion led to C–O bond formation followed by the second hydrogen abstraction in the next step. The mobility of lattice oxygen is more important in both acrolein selectivity and propylene conversion.

3. Bio-based acrolein production

3.1. Gas-phase dehydration of glycerol to acrolein

Acrolein is a significant and flexible chemical intermediate for the production of super-absorber polymers (e.g. sodium polyacrylate (SAP)), detergents, and particularly acrylic acid esters. A sustainable and economical acid dehydration of glycerol to acrolein emerged as a new approach to substitute conventional petrochemical process in the presence of propylene oxide and Bi/Mo-mixed oxide catalysts.

Attempts to produce acrolein by dehydration of glycerol in the gas phase could be traced a long time ago. Schering–Kahlbaum AG at 1933 [91] patented the first catalytic (phosphates of Cu or Li) dehydration of glycerol in the gas phase by 80 mol% acrolein yield at 573–873 K reaction temperature. However, high cost of glycerol in the past was considered as the main reason for this process to remain undeveloped until 15–20 years ago when cheaper glycerol was available in the market as a byproduct in the biodiesel production process. New generation of research on glycerol dehydration was initiated by Neher et al. [92,93] who compared application of well-defined Hammett acidities (HAs) of lithium phosphate catalysts. 75% Acrolein selectivity obtained with 100% glycerol conversion over alumina supported phosphorous acid catalyst at 573 K temperature. In addition, Neher and Haas [94] reported 70.5% acrolein yield by alumina supported phosphorous acid catalyst. As a result, there is dramatic increase in the interest of glycerol as a high value sustainable source for value-added chemicals. Application of various types of catalysts in dehydration of glycerol into acrolein has been reported recently including heteropoly acids, zeolites, mixed metal oxides, phosphates and pyrophosphates.

Table 1

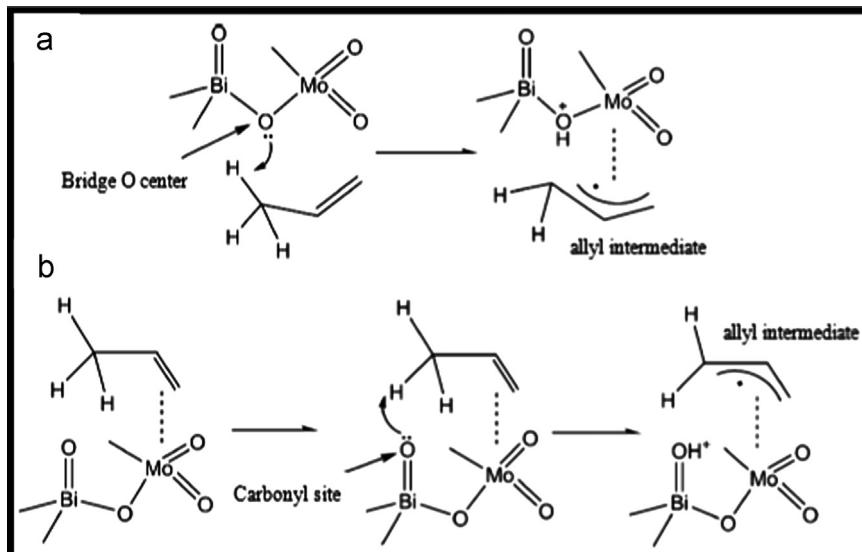
Various studies on petroleum-based acrolein production [62].

Catalyst	Feed ratios ^a	Contact time (s)	T (K)	Conversion (%)	Selectivity (%) ^b	Ref
$\text{Mo}_5\text{VW}_{1.5}\text{Te}_{0.5}\text{Sb}_2\text{Sn}/\text{Bi}$ oxide	I/O/steam = 1:1.6:6	3	723	66.5	N.A. ^c	[63]
Te-V-W-As/Sn-(Sb) oxide	I/O/steam = 1:6:3	4.9	643	65.6	69.9	[64]
Sn-Sb-U oxide	I/O/N = 5:7.5:87.5	3.5	703	89	81	[65]
$\text{SnSb}_2\text{VFe}_{0.5}\text{Bi}_{0.01}$ oxide	I/O/N/steam = 1:12:67:15	3	543	62.3	72.8	[66]
$\text{Cr}_2\text{Al}_{0.7}\text{Mo}_{0.35}$ oxide	I/air/steam = 4:50:46	4	657	95	83.3	[67]
$\text{Ni}_{10}\text{Co}_{0.3}\text{FeBiPMo}_{12}\text{O}_{57}$	I/air/steam = 1:10:4.1	1.8	633	90	93.1 ^d	[68]
$\text{Ni}_{4.5}\text{Co}_4\text{FeBiP}_{0.08}\text{Mo}_{12}\text{O}_{31}$	I/air/steam = 1:10:6	4	583	95.5	82.8	[69]
$\text{NiCo}_3\text{Fe}_2\text{BiAs}_{1.5}\text{K}_{0.2}\text{Mo}_{12}\text{O}_{48.35}$	I/air/steam = 1:10:5	1.5	578	94	93	[70]
$\text{NiCo}_3\text{Fe}_2\text{BiP}_2\text{K}_{0.2}\text{Mo}_{12}\text{O}_{49.6}$	I/air/steam = 1:10:5	1.5	578	96	88	[71]
$\text{Mo}_{12}\text{Bi}_{0.1-7}\text{Mg}_{0.5-12}\text{Fe}_{0.1-7}\text{Mn}_{0-5}\text{O}_{25-80}$	I/air/steam = 4.5:53:42.5	9	643	94.8	73.7	[72]
$\text{Ni}_{10.5}\text{FeBiMo}_2\text{O}_{54}$	I/air/steam = 1:10:6	4	543	95.8	69.9	[73]
Mo-Bi-Fe-Mn-X oxide ^e	I/air/steam = 6:42.8:51.2	2.4	613	91.3	80.4	[74]
Mo-Co-Fe-Bi-X-O ^f	I/air/steam = 1:12:7	2.4	623	90.8	81.5	[75]
B-W-Co-Bi-Fe-Mo-Si-M-O ^g	I/air/steam = 1:14:10	6	603–623	99.6	73.7	[76]
$\text{Mo}_{10}\text{Co}_8\text{Fe}_2\text{Bi}_{0.9}\text{V}_{0.05}\text{K}_{0.05}$ oxide	I/air/steam = 1:10:4	1.6	603	63–92	70–95	[77]
$\text{Co}_4\text{BiFeW}_2\text{Mo}_{10}\text{Si}_{1.35}\text{K}_{0.06}$ oxide	I/O/steam:N = 7:12.6:10:70.4	2.25	593	96.2	86.6	[78]
Co-K-Mo-W-(P) oxide	I/air/steam = 1:10:8	25	623	84.9–86.9	83.1–87.7	[79]
$\text{Mo}_{12.25}\text{Bi}_1\text{Fe}_3\text{Co}_{0.1}\text{Cs}_{0.1}$	I/O/steam = 1:10:3:20:70–96	N.A. ^c	633	96.0	88.75	[80]
Bi-Mo-Fe-Ni-Si oxide	I/O/N = 1:1–20:1–20	3	633	87.3	96.5	[81]
Mo-Bi-Fe-Co-(Ni)-X oxide ^h	I/O/steam:N = 1:1.6 :2.3:4.9	N.A. ^c	583	> 97	87.63	[82]

^a Molar ratio is used (mol/mol); I: propylene.^b Selectivity is defined as the molar ratio between the carbon in the acrolein produced in the reaction and the carbon in the converted propylene.^c Not available.^d Acrolein + acrylic acid.^e X = K, Rb, and/or Cs.^f X = Sn or Sn with Al, Ni, W, Cr, In, Nb.^g M = alkali metal.^h X = Cs and/or K.**Table 2**

Various approaches for improvement of petroleum-based acrolein production.

No	Modified process	Advantages	Ref
1	Circulating fluidized bed reactor & Neural network modeling and simulation of fluidized bed reactor	Application of higher propylene concentration with less restrictions of the upper explosion limit, that led to higher mass and heat transfer rate, higher turndown ratio, easy catalyst removal and addition.	[83,84]
2	Application of heat-transfer CO_2 during the operation of multi-tubular reactor	(1) Enhanced the production by 14% (2) The heat transfer effect study in both experimental and theoretical application (3) This process provided a huge range for safe reaction inlet and coolant temperature.	[85]
3	Catalytic wall reactor was proposed in a specific reaction temperature	The kinetic and mechanism of partial oxidation of propylene to acrolein was significantly studied to reach more reliable results.	[61,86]
4	Application of membrane reactor	(1) Increase the acrolein yield (2) Lower partial oxygen pressure led to elimination of CO_x production	[87]

**Fig. 7.** Mechanisms of allyl intermediate formation (initial/rate-determining steps of the partial oxidation of propylene).

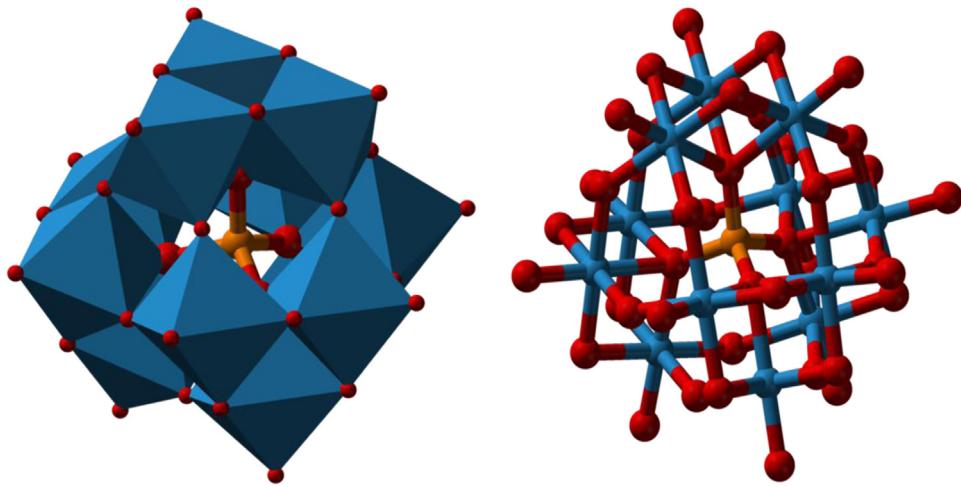


Fig. 8. HPA catalyst structure.

3.1.1. Application of supported heteropoly acid catalysts

The application of heteropoly acids (HPAs) catalyst has attracted much attention due to both biodiesel and value-added chemical production from glycerol. HPAs can be used as acid and oxidation catalysts in both solid and liquid states. HPAs are highly stable against humidity and air, low toxicity, highly soluble in polar solvents (water, acetones, and lower alcohols), produce less quantities of residues than mineral acids, less corrosive, and finally these are much safer than all other catalysts [95]. $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ are three commercially available heteropoly acids. The tungstophosphoric acid (TPA) is a common HPA catalyst that is widely used (Fig. 8). It is the highest acidic Keggin type HPAs when impregnated on various supports such as hydrous zirconia (HZ), silica (Si), alumina (Al), and activated carbon (AC). In addition, it has higher thermal stability up to 673 K and easier to synthesize compared to other HPAs.

One possible approach to obtain better glycerol dehydration to acrolein performance is to use supported inorganic acids such as heteropoly acids (HPAs) and phosphorous acid. Characteristics such as acidity, effect of support on active phase, dispersion of active phase, and pore size distribution of support have been reported to exert significant influence on catalyst activity [93,94,96].

Chai et al. [97,98] investigated glycerol dehydration to acrolein over silica and zirconia supported HPA catalysts. The results indicated that zirconia supported HPA (PW/ZrO_2) with 58% acrolein yield was more efficient than silica supported HPA (PW/SiO_2) with only 10% yield. However, catalyst deactivation was the main problem in both cases. Researchers concluded that catalyst support nature is influential for dispersing of Keggin-type active phase and thermal stability. Furthermore, the main factor that controls the selectivity and activity of HPA catalyst is the Keggin-anion density at the surface of the support. This factor is reported by Ning et al. [99] who utilized silicotungstic acid catalyst supported by activated carbon ($HSiW/AC$). They obtained phenomenal results of 62% acrolein yield at 93% glycerol conversion and only 8% by product (acetol) selectivity.

Katryniok et al. [100] investigated glycerol dehydration to acrolein in the presence of silicotungstic acid catalyst supported on SBA-15 modified by zirconia grafting. Grafting modified electronic interaction between HPA and support. The results showed that the interaction between heteropoly anion and zirconia reduced the Bronsted acidic site strength which finally led to higher and long term catalyst stability. They also identified the amount of zirconia, support pore size, and active phase amount as the three main variables which have significant impact on catalytic

performance. The best catalyst was 8 nm pore size SBA-15 calcined at 923 K, grafted by 20 wt% zirconia and impregnated with 20 wt% silicotungstic acid. The highest acrolein yield was 71% and 69% after 5 h and 24 h reaction time, respectively. Alhanash et al. [101] also reported that the main concern is the quantity of grafted zirconia which could reduce acrolein selectivity due to formation of undesired Lewis acidic sites on the catalyst.

Erfel et al. [102] reported glycerol dehydration to acrolein over phosphomolybdic ($H_3PMo_{12}O_{40} \cdot xH_2O$) and vanado-phosphomolybdic ($H_4PMo_{11}O_{40} \cdot xH_2O$). The Si/Al ratios for Keggin structure were 0.21 and 0.32, respectively while the Si/Al ratio for Al-MCM-41 was 10. Both UV-vis-DR and EPR spectra analysis were used to evaluate the reaction results. There were two different feeds of glycerol with 1/14.1/36.8/0.68 or 1/14.1/36.8/0.0 of $N_2/H_2O/O_2$ ratios at 553 K reaction temperature. They reported low selectivity (25%) since the Keggin structure was partially destroyed by impregnation on $SiO_2-Al_2O_3$ supports. Erfel and his co-workers concluded that the presence of oxygen in the feed and vanadium ions in the catalyst enhanced catalyst stability by keeping the metal ions in a high oxidized state and the carbon deposits in a low condensed state. Finally, vanado-phosphomolybdic (HPVMo) and phosphomolybdic (HPMo) supported by Al-MCM-41 exhibited the highest acrolein selectivity due to its lowest surface acidity, largest surface area, smallest mean pore diameter, and highest molybdate dispersion. The textural properties of various catalysts in this research are listed in Table 3.

Dubios et al. [103] evaluated application of phosphotungstic (PW) and silicotungstic (SiW) acid salts by partial or complete substitution of metal cations instead of HPAs protons. They used various elements cesium (Cs), rubidium (Rb), calcium (Ca), and bismuth (Bi) and transition metals (zirconium (Zr), lanthanum (La), iron (Fe), and hafnium (Hf)). The results indicated that the partially neutralized rubidium (Rb) and cesium (Cs) for both PW and SiW based catalysts required lower reaction temperature (533–553 K) than other complete neutralized group (573–623 K). Moreover, these groups of catalysts represented significant increase in acrolein selectivity up to 90% in contrast with 50–70% selectivity over other catalysts. The $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$ catalyst demonstrated the highest acrolein yield (93.1%). Authors also reported that oxygen co-feeding has a significant effect in this study as acrolein yield reduced to 40% without oxygen co-feeding. Alhanash et al. [101] obtained the highest acrolein yield (98%) over cesium salts of PW acids. However, the 98% yield lasted only within the first few hours of reaction after which the catalyst deactivated very fast. Martin et al. [95] mentioned that application

Table 3

Surface and pore characteristics of various catalysts [102].

Catalyst	S_{BET} (m^2/g)	Mean pore diameter (nm)	Bronsted sites ^b	Lewis sites ^c
Si/Al-0.21 ^a	349	8.34	2.2	8.8
HPMo/0.21	300	7.90	7.0	10.3
HPVMo/0.21	259	8.00	10.2	14.3
Si/Al-0.32 ^a	333	11.08	5.4	–
HPMo/0.32	235	11.27	4.9	3.3
HPVMo/0.32	206	11.46	7.8	6.7
Al-MCM-41 ^a	857	2.84	1.0	1.5
HPMo/MCM	611	2.75	3.7	6.7
HPVMo/MCM	408	2.81	4.2	8.4

^a Pure supports.^b Derived by normalizing the FTIR band area at 1540 cm^{-1} on S_{BET} .^c Derived by normalizing the FTIR band area at 1450 cm^{-1} on S_{BET} .

of alkali metals such as K^+ , Cs^+ , and Rb^+ , into HPAs led to lower water solubility and simultaneously enlarged the specific surface area.

Shen et al. [104] studied gas phase dehydration of glycerol catalyzed by rutile TiO_2 -supported HPAs. The incipient wetness impregnation method was employed to synthesize TiO_2 -supported heteropoly acid catalysts. Silicotungstic (HSiW), phosphotungstic (HPW), and phosphomolybdic (HPMo) acids were used as active compounds. It was found that in the rutile TiO_2 supported silicotungstic acid, the surface areas of HSiW- TiO_2 -5, HSiW- TiO_2 -10, and HSiW TiO_2 -20 catalysts decreased from 12.9 to 12.5. Similar results were reported for TiO_2 -supported phosphotungstic and phosphomolybdic acid catalysts. The acrolein selectivity was influenced by reaction temperature and HPAs type and loading. Among all, TiO_2 -supported silicotungstic acid (20 wt%) catalyst exhibited the highest catalytic activity with an acrolein selectivity of 80 mol% and 99% of glycerol conversion at 553 K reaction temperature and atmospheric pressure.

Atia et al. [105] synthesized a series of supported silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) catalysts from selected silica with particle size in the range of 315–500 μm and pore diameter 11 nm and also alumosilicate support (average pore diameter 5 nm). The Brønsted acidic sites were modified by addition of alkaline metals such as cesium (Cs), potassium (K), and lithium (Li). The unmodified supported HSiW catalysts (with the maximum number of protons) exhibited the highest activity, which indicated that activity is strongly connected with (Bronsted) acidity. In their study, physico-chemical characterization of the catalysts was carried out using various methods. It was found that the nature of the alkaline metal is significant for increasing the specific surface area by metal ion radii and dispersion of active compound created by silicotungstic acid (HSiW) and alkaline metal on the supported surface. Surprisingly, the acidic properties did not depend on the nature of the alkaline metal. Among the tested catalysts, where alkaline metals Li, K and Cs were impregnated in a second step onto supported silicotungstic acid, Li modified HSiW catalyst gave the best performance with 70% acrolein selectivity and complete glycerol conversion at 573 K. However, Cs modified catalyst exhibited the least acrolein selectivity and conversion over the complete range of reaction temperature, due to the formation of larger crystalline phases. Unfortunately, they did not investigate the long-term stability of the catalysts.

Haider and his co-workers [106] dehydrated glycerol to obtain acrolein using rubidium- and cesium-doped silicotungstic acid (Cs/STA and Rb/STA) catalysts. The prepared catalysts were in different dopant metal cations concentrations while the concentration of HSiW was kept constant. They reported 94–96% acrolein selectivity. However, these unsupported catalysts were not stable for prolonged reactions even with less glycerol concentration (0.5 wt %) in the feed flow. In addition, researchers evaluated the effect of

supported alpha-(Al_2O_3 -1) and theta-delta (Al_2O_3 -2) alumina on the Cs/STA and Rb/STA catalysts. 90% Acrolein selectivity at complete glycerol conversion was obtained over cesium-doped silicotungstic acid supported on theta-delta alumina (Cs/STA-2) during 90 h on stream. The group of researchers also claimed that this type of catalyst possessed the most stable silicotungstic acid (STA) derived catalyst without requiring oxygen co-feeding to increase stability. Moreover, the Keggin structure and acidity of active sites were considered as the main reasons for high acrolein yield production.

Zhao et al. [107] produced acrolein by dehydration of glycerol in a fixed-bed quartz reactor over montmorillonitic clay (MMT) activated by sulfuric acid catalyst. Various sulfuric acid concentration range (5–40 wt%) was utilized for montmorillonite activation. Researchers used different characterization methods (XRD, FTIR, and NH_3 -TPD) for evaluation of the sulfuric acid treatment effect on the catalyst structure. They also investigated the effect of various reaction parameters such as feed rate, glycerol concentration, and reaction temperature on catalyst activity. The acceptable 44.9 wt% acrolein yield at 54.2% glycerol conversion was achieved at optimum condition of liquid hourly space velocity (LHSV) of 18.5 h^{-1} , 10 wt% glycerol concentration, 10 ml/min flow rate of N_2 carrier gas, and 593 K reaction temperature. The key factor in this reaction was the H^+ in the interlayer space of acid-activated MMT catalyst due to reformation of $\text{H}^+ \text{-MMT}$ instead of $\text{Ca}^{2+} \text{-MMT}$ by ion exchange reaction during activation process.

Kim et al. [108] investigated glycerol dehydration to acrolein in the presence of silicotungstic acid (HSiW) catalyst supported with various metal oxides (TiO_2 , ZrO_2 , SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, AC, CeO_2 , and MgO). Generally, the conversion of glycerol increased with enhanced acid site concentrations. The total amount of acid sites was in the following order: HSiW > $\text{SiO}_2\text{-Al}_2\text{O}_3$ > HSiW/ $\gamma\text{-Al}_2\text{O}_3$ > HSiW/ CeO_2 > HSiW/AC > HSiW > ZrO_2 > HSiW/ TiO_2 > HSiW/ SiO_2 > HSiW/ MgO . The HSiW catalyst supported by ZrO_2 and $\text{SiO}_2\text{-Al}_2\text{O}_3$ gave the highest selectivity of 58.1% and 58.0%, respectively, among all the catalysts. Kim et al. [108] reported the successful regeneration of HSiW/ ZrO_2 catalyst due to elimination of carbon species by oxygen stream at 823 K.

Table 4 tabulates other studies which have utilized HPA catalysts for glycerol dehydration to acrolein. The results reveal that higher catalytic activity for acrolein production depends on the medium acid site and also the nature of the acidic sites (Bronsted). In addition, the long-life stability of catalyst is related to the catalyst supports such as metal oxides (Al_2O_3 , ZrO_2 , and TiO_2) or metals (K, Li, Cs, Pt, Rb, and Pd).

In summary, all these studies demonstrated that heteropoly acid catalysts have high ability for adjustment by modifying their central atoms with various compounds. Researchers have attempted to increase the catalytic activity and long-life stability of the catalysts to achieve the highest acrolein yield. As mentioned before, the Cs/HPW catalyst displayed the best ever reported acrolein yield of 98% for glycerol dehydration in the gas-phase. However, the main drawback of the catalyst was that its activity lasted for only a few hours as it deactivated very fast. However, the cesium-doped silicotungstic acid supported on theta-delta alumina (Cs-STA-2) showed 90% acrolein selectivity at 100% glycerol conversion during 90 h on stream. In addition, 86% acrolein selectivity at complete glycerol conversion was achieved over 50%HPW/Cs-SBA catalyst with 170 h of stability. These catalysts are the best samples for both high stability and catalytic activity among all the supported heteropoly acid catalysts.

3.1.2. Application of supported zeolite catalysts

Zeolite is a micro-porous, alumino-silicate mineral conventionally used as commercial adsorbents due to its unique porous

Table 4

Application of HPA supported catalysts for glycerol dehydration to acrolein.

Prepared catalyst	The best catalyst	T (K)	TOS (h)	Con (%)	S _{AC} (%) ^a	Reason for catalyst activity	Ref
WO ₃ –ZrO ₂	HPW–TiO ₂	553	–	100	74	The total acidity and the nature of acidic site (Bronsted)	[109,110]
HPW–WO ₃ –ZrO ₂							
HPW9TiO ₂							
Cs–PW	50%HPW/Cs-SBA	573	20	100	86	Medium acidity of catalyst and high stability (170 h) due to SBA-15 application	[111]
50%HPW–SBA							
30–70%HPW/Cs-SBA							
5–60%CsPW–Nb	20%CsPW-Nb-500	573	11	96	80	Nb ₂ O ₅ helped to retain the Cs-PW Keggin structure and Medium acid sites at high temperature	[112]
Calcined at 400–700 °C							
Pt/(30–40%)HPW/MCM-41	Pt/35%HPW/Zr-MCM-41	623	5	87	81	Higher Bronsted acidic site compare to Lewis acidic site	[113]
Pt/(30–40%)HPW/Zr-MCM-41							
20%DTP/K-10	20%DTP/HMS	498	4	94	80	The Bronsted acidic site on DTP and free hydroxyl group, hydrophilicity, and neutral nature of hexagonal mesoporous silica (HMS)	[114]
20%DTP/HMS							
20%DTP/OMS							

^a Acrolein Selectivity.

characteristics. These materials have been used in various applications with a global market of several million tons annually. There are 206 zeolite frameworks have been identified until October 2012 [115] which includes ion-exchange beds in water purification, gas separator, catalyst in petrochemical, nuclear and biogas industries and heating (solar thermal collectors). The largest zeolite application is in detergent production.

Dubois et al. [116] patented two well-known zeolite type catalysts (ZSM-5 and β -zeolite) for acrolein production by dehydration of glycerol. They obtained 57% acrolein at 100% glycerol conversion, but only 39% acrolein yield at 79% glycerol conversion at the same temperature of 573 K for β -zeolite and HZSM-5, respectively. Besides, Zhuang et al. [117] evaluated the application of other types of zeolites catalyst (MCM-49, MCM-22, MCM-56, and ZSM-11) for dehydration of glycerol with a range of 70–85% acrolein yield. More importantly, these catalysts exhibited high stability even after 400 h reaction time.

In addition, Okuno and Coworkers [118] patented various metallo-silicate catalysts (alumino-, gallo-, and ferro-silicate) with an MFI structure (typical zeolite structure with 3D porous network). However, ferro-silicate exhibited lower selectivity because of their higher redox properties. In contrast, alumino-silicate demonstrated the best performance with 65% acrolein selectivity. They also examined catalysts with different Si/Al ratios to control acidity. The results indicated that Si/Al ratio equal to 28 was the best with 63% acrolein yield at 92% glycerol conversion while 61% acrolein yield at complete glycerol conversion was achieved with Si/Al ratio of 200.

Kim et al. [119] evaluated the effect of various reaction parameters such as Si/Al ratio, reaction temperature and water content in gas-phase dehydration of glycerol in the presence of H-ZSM-5 and Na-ZSM-5 catalysts. They prepared various Si/Al ratios (30, 60, 150, 500, and 1000) for HZSM-5 and Si/Al ratio of 23 for Na-ZSM-5 catalysts. The highest acrolein selectivity of 63.8% was obtained by HZSM-5 with Si/Al ratio of 150 at 588 K reaction temperature. The NH₃-TPD and FTIR characterization results revealed that by increasing the Si/Al ratio the acid strength increased. Thus, the catalytic activity was low in the case of HZSM-5. In addition, they found that the amount of absorbed water and its binding strength reduced with increasing Si/Al ratios. Na-ZSM-5, on the other hand, exhibited the lowest catalytic activity among all catalysts samples due to its weaker acid sites and high water adsorption on the active site. The rest of the experiments revealed that as more water is fed the acrolein yield increased up to 53.2%. Meanwhile, higher temperature up to 613 K registered a slight surge in acrolein yield of 58.3% compared to 48.4% at 588 K.

Jia et al. [120] investigate effect of HZSM-5 with various Si/Al ratios (20, 27, and 200) and compared the application of nanocrystalline HZSM-5 with Si/Al ratio of 65 and bulk HZSM-5 for gas phase dehydration of glycerol. The results indicated that nano-size catalyst significantly improved the catalytic activity even in the presence of crude glycerol. In addition, they synthesized a series of zeolite catalysts with specific particle size and various Bronsted acidic site densities by controlling the proton exchange degree in H_xNa_{1-x}ZSM-5. In this case, results revealed that higher Bronsted acidic site was suitable for acrolein production. Finally, it was concluded that nano-size HZSM-5 with high Si/Al ratio was the best choice for gas phase dehydration of glycerol due to its stronger Bronsted acidic sites which facilitated the mass transfer rate better.

Zhou et al. [121] used micro- and meso-porous ZSM-5 catalyst which was synthesized by dual templates in one-step crystallization route in glycerol dehydration to acrolein. They compared the catalyst activity of ZSM-5, MCM-41, solid phosphoric acid, and the mixture of ZSM-5 and MCM-41 with the synthesized catalysts. The results revealed that the highest 73.64% acrolein yield at 98.27% glycerol conversion was obtained over micro- and meso-porous ZSM-5. However, they concluded that meso-porous ZSM-5 was more suitable than micro-porous since no diffusional limitation was observed for the meso-porous material.

Glycerol gas-phase dehydration was performed by Kim et al. [122] over different H-zeolites including H-ferrierite, H- β , HZSM-5, H-Y and H-mordenite with various Si/Al ratios. Different characterization techniques were employed to characterize the catalysts. XRD revealed that primary crystallite size of the H-zeolites decreased in the following order: H-ferrierite > H-Y > H-ZSM-5 ~ H-mordenite > H- β . The SEM images for the zeolites revealed that the zeolites exhibited different morphologies with different particle sizes. As a consequence of agglomerated particles, they could not determine the particle size accurately.

The glycerol conversion at 588 K was in the following order: silica-alumina > H- β (25) > H- β (27) > γ -Al₂O₃ > H-mordenite (20) > H-ferrierite (55) > H-ferrierite (20) > H-ZSM-5 (23) ~ H- β (350) > H- β (38) ~ H-Y (5.1). Among all these catalysts, H-ferrierite (55), exhibited the highest acrolein selectivity being 77.1% at the optimum conditions: 91.7% water content, 23.4 mmol/h glycerol feed flow rate, 0.3 g catalyst weight, and 613 K reaction temperature. The effect of reaction temperature and contact time was also investigated. It was found that in the case of H- β (25), the acrolein selectivity increased with increasing reaction temperatures up to 588 K and then decreased as the reaction temperature was further increased, which was in good

agreement with the results obtained over H-ZSM-5 [119]. The acrolein selectivity was increased monotonically with increasing reaction temperatures over H-ferrierite (55). On the other hand, the glycerol conversion increased with longer contact time while the acrolein selectivity gradually decreased and acetaldehyde selectivity increased by increasing time-on-stream. No noticeable change in the 1-hydroxyacetone selectivity was observed during the reaction. In addition, researchers concluded that the morphology of a solid catalyst is the key factor in glycerol conversion since the majority of H-zeolite micro-pores were filled by carbon sources at the beginning of reaction which seriously decreased the catalytic activity.

In a successful attempt Witsuthammakul and Sooknoi [123] produced acrylic acid in a single reactor with subsequent oxidation of the glycerol dehydrated products. Different catalysts (HZSM-5, H β , H-Mordenite and HY) were tested and their selective dehydration of glycerol to acrolein was studied at 548–673 K. They also studied the effect of mixed oxides loading and composition as well as oxygen concentration. They found that the acrolein conversion increased when the mixed oxides loading surged from 20 to 50 wt % as a result of increased active phase of the catalysts. The results indicated that HZSM-5 with medium pore size exhibited the highest (81 mol%) acrolein selectivity at complete glycerol conversion with 10–30% glycerol concentration and 573 K reaction temperature. They also evaluated the application of vanadium-molybdenum oxides catalyst for the second bed process for acrylic acid production and proposed a reaction pathway for this process (Fig. 9).

Possato et al. [124] examined the effect of desilication methodology to increase the glycerol conversion and minimized diffusion limitations by formation of secondary pore in zeolite crystals. In their study, glycerol conversion increased due to reduced surface acidity strength improved mesoporosity and glycerol accessibility to the active sites. In fact, the main advantage of this process is less blocked micro-pores and catalyst longer stability. Table 5 summarizes some recent studies on application of zeolite catalysts in glycerol dehydration to acrolein.

In conclusion, total acidity is the most important factor that enhances the catalytic activity of supported zeolite catalysts. The acidity can be controlled by changing the Si/Al ratio, applying transition metal oxides or by modifying the catalyst surface (ion-exchange). As mentioned before, Lourence et al. [128] obtained 92.6% acrolein selectivity with 100% glycerol conversion at 573 K reaction temperature which is the highest ever reported acrolein selectivity over zeolite catalysts for dehydration of glycerol in gas phase. However, the value is still less than HPA catalysts. Most probably the nature of the acidic sites related to the HPAs or the Keggin structure of HPAs are the main reasons for higher activity. These characteristics are motivation for more studies to be conducted in search to find the best catalyst for glycerol dehydration to acrolein.

3.1.3. Application of mixed metal oxides, phosphates, and pyrophosphates catalysts

Mixed oxides, phosphates, and pyrophosphates are also widely being used in dehydration of glycerol to acrolein. Metal oxide

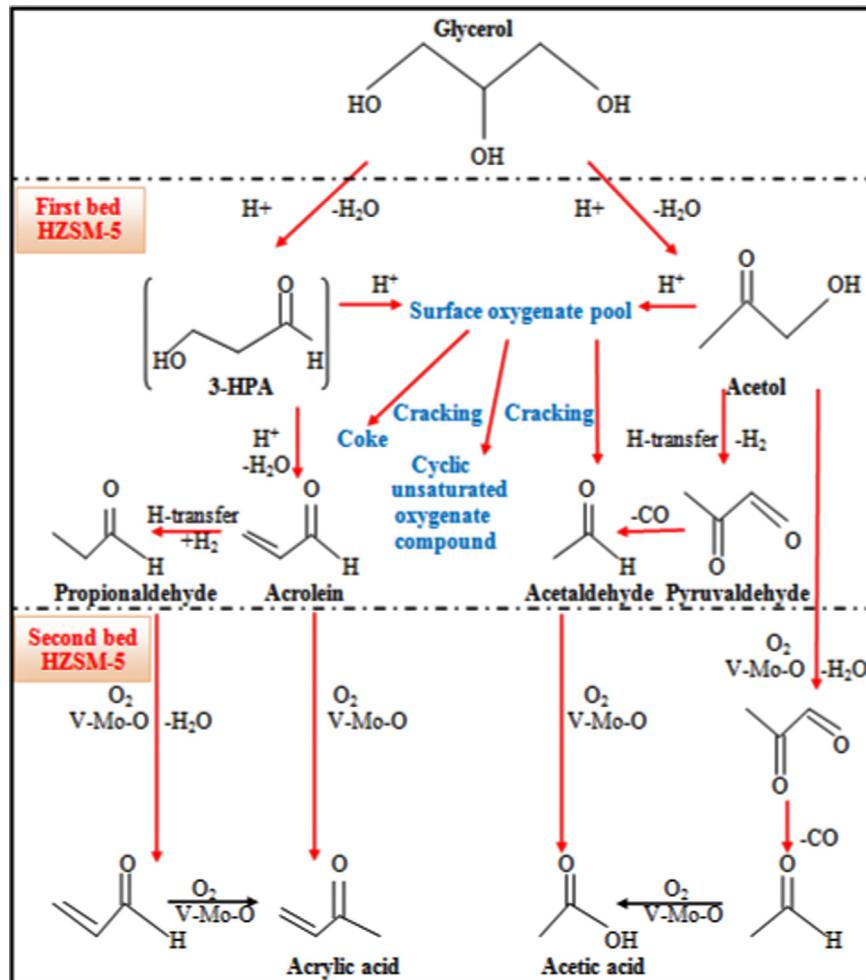


Fig. 9. Glycerol dehydration and subsequent oxidation to acrylic acid.

Table 5

Recent studies related to application of zeolite catalysts for dehydration of glycerol to acrolein

Prepared catalyst	The best catalyst	T (K) ^a	TOS (h) ^b	Con (%) ^c	S _{AC} (%) ^d	Y _{AC} (%) ^e	Reason for catalyst activity	Ref
MCM-22 (30–80 Si/Al ratios)	MCM-22 (30)	593	2	99.75	50.05	49.92	High surface area and high acid site	[125]
H β	LCH- β	548	7	51.05 (95) ^f	65.5 (87.2) ^f	33.4 (82.9) ^f	H β and LCH- β catalysts had similar acidity, but strength distribution was different. LCH- β contained more medium strength acidic site.	[126]
LCH- β								
LCL- β								
–	HZSM-5	773	1.5	100	–	68	The 3 staged reactor for dehydration, hydrogenation, and upgrading stages in series used for light olefin production from glycerol. The highest ever reported light olefin yield (70%) obtained in this research.	[127]
SBA-15 SBA-SO ₃ H (1–3)	SBA-SO ₃ H (1)	573	3	100	92.6	–	Large pore size dramatically enhanced catalyst activity and high acid site density decreased acrolein selectivity.	[128]

^a Reaction temperature.^b Time on stream.^c Reaction conversion.^d Acrolein selectivity.^e Acrolein yield.^f Numbers in bracket related to first 0.5 h of reaction.

catalysts such as niobium oxide (Nb_2O_5), tungsten oxides (WO_3), and aluminum oxide (Al_2O_3) have been widely used in chemical processes. The most important factors about metal oxide catalysts is their synthesis method (especially calcination temperature) and their binary or tertiary combinations which have detrimental impact on the final catalyst physicochemical properties. In fact, this group of catalysts has many parameters for evaluation and investigation during the optimization of catalytic activity.

Chai et al. [129] investigated acrolein production by gas phase dehydration of glycerol in the presence of niobium oxide (Nb_2O_5) catalyst at 588 K reaction temperature. The effect of various calcination temperatures (623, 673, 773, 873, and 973 K) on acidity, crystal structure, and catalyst texture was evaluated. The results indicated that acrolein selectivity and glycerol conversion are significantly related to the strong catalyst acid sites. Calcination temperatures of 623 and 673 K illustrate stronger acid sites compared to calcination temperatures beyond 773 K. In fact, 673 K calcination temperature registered the highest fraction of strong acid site (Hammett acidity function range of -8.2 to -3.0) that dramatically enhanced the acrolein selectivity up to 51 mol% at 88% glycerol conversion. The deactivated catalysts could be regenerated by simple air flow treatment at similar reaction temperature. In another study, Tao et al. [130] expanded their research by application of various acidic binary metal oxides (SnO_2-TiO_2 , SnO_2-ZrO_2 , $TiO_2-Al_2O_3$, SiO_2-TiO_2 , ZrO_2-SiO_2 , $ZnO-TiO_2$, and TiO_2-ZrO_2) in gas phase glycerol dehydration to acrolein at 588 K. Similar to Chai et al. [96] the highest acrolein selectivity from aqueous glycerol (36.2 wt%) was obtained on strong acid site range of $-8.2 \leq H_0 \leq -3.0$. The micro-pores on the catalyst surface had negative influence on acrolein selectivity due to the formation of secondary reactions. The results demonstrated that 10 mol% $TiO_2-Al_2O_3$ and 50 mol% TiO_2-ZrO_2 , calcined at 873 K and 823 K, respectively rendered the highest catalytic activity.

Suprun et al. [131] investigated the gas phase dehydration of glycerol to acrolein over alumina-phosphate ($Al_2O_3-PO_4$), titanium-phosphate (TiO_2-PO_4), and silica alumina-phosphates (SAPO-11 and SAPO-34) in the presence of water at 533 K. The results suggested that acrolein selectivity and glycerol conversion were highly dependent on the textural and acidity properties of the catalyst. Silica alumina-phosphate (SAPO-34) exhibited the highest acrolein selectivity of 72% at 59% glycerol conversion among all catalysts at 60 min reaction time. Unfortunately, all catalysts deactivated rapidly in this research.

Wang et al. [132] utilized three types of vanadium phosphate oxide (VPO) catalysts ($VOPO_4 \cdot 2H_2O$, $VOHPO_4 \cdot 0.5H_2O$, and

$(VO)_2P_2O_7$) in gas phase dehydration of glycerol to acrolein. The effect of different reaction parameters such as ratio of oxygen to glycerol (0, 1.1, 4.5, 9.1, and 13.6), reaction temperature (523, 548, 573, 598, and 623 K), and space velocity rate (WHSV) (20.5, 10.2, 5.1, and 2.6) on catalytic activity was evaluated. The results revealed that hemihydrates $VOHPO_4 \cdot 0.5H_2O$ oxide was the best catalyst with 66% acrolein selectivity and complete glycerol conversion at 573 K and only 14% acetaldehyde selectivity as the main by-product. The oxygen flow had positive effect since catalyst could be maintained in an oxidized state and the side products formation such as coke were significantly reduced. The XRD, IR, and TGA characterization methods demonstrated that catalyst was highly stable during the reaction. In another study, Wang et al. [133] applied temperature treatment (773–1173 K) on vanadium pyrophosphate oxides (VPO) catalyst. Interestingly, the temperature treatment could change the textural morphology, crystalline stacking order, acidity, and surface P/V ratio. The 1073 K temperature treatment registered the highest (95%) selectivity of all products (e.g. 64% acrolein) at complete glycerol conversion. The effect of oxygen flow was evaluated and the reaction with oxygen dramatically decreased the formation of by-products with no coke formation. Similarly, Dubois [134] continued the study by application of pyrophosphate using boron (B) as cations. The boron-containing compounds exhibited 77.8% acrolein yield. Liu and coworkers [135] evaluated the application of lanthanum (La), neodymium (Nd), and cerium (Ce) in glycerol dehydration. Generally, all these catalysts exhibited similar catalytic performances. For example, 80% acrolein yield at 773 K calcination temperature was achieved over $Nd_4(P_2O_7)_3$. They also concluded that the catalyst acidity was enhanced by higher calcination temperature. This is in agreement with the results provided by Wang et al. [133].

Deleplanque et al. [136] used iron phosphates ($Fe_x(PO_4)_y$) instead of pyrophosphates with precipitation or hydro-thermal reaction preparation methods for dehydration of glycerol. They obtained 92% acrolein yield at 100% glycerol conversion at 553 K with hydro-thermal synthesis. The catalyst deactivated after 25 h reaction time; however, oxygen (O_2) flow could reduce the hydroxyl acetone and carbon deposits. Besides, acrolein, CO, and CO_2 yields also decreased to 62.5%, 4.7%, and 8.2%, respectively. Dubios [137] also employed the idea of doping the phosphate species by potassium (K), strontium (Sr), and cesium (Cs). But, they obtained only 72.2% acrolein yield by cesium (Cs), which was still less than the 92.1% acrolein yield in Deleplanque et al. [136] research. This idea was extended by Matsunami et al. [138] who applied phosphate modified silica with alkali salts for glycerol

dehydration. They reported only 67% yield which was lower than 92.1% acrolein yield in reaction without oxygen flow.

Patience et al. [139] used cerium-doped FePO_4 catalyst for dehydration of glycerol to acrolein in the gas phase. The reaction conditions were 20–40 wt% glycerol concentration, 593–653 K reaction temperature in 60 min reaction time. Co-feeding of oxygen (1–5 vol%) effect was also examined for regeneration of catalyst. The best 83 g acrolein $\text{h}^{-1} \text{kg}_{\text{cat}}^{-1}$ space time yield (STY) was obtained at 635 K before regeneration step. Oxygen co-feeding improved coke reduction but selectivity suffered in proportion to the oxygen fed, because, all the oxygen transformed to CO_2 . Researchers also determined the first order reaction rate for this study.

Lauriol-Garbay et al. [140] reported that zirconium and niobium mixed oxides exhibited approximately 72% acrolein selectivity with nearly complete glycerol conversion at 573 K in the presence of water. HZSM-5 and ZrW-DKK registered more selectivity than ZrNbO ; however, HZSM-5 and ZrW-DKK completely deactivated after 24 h. ZrNbO catalysts exhibited 82% conversion efficiency after 177 h on stream while its acrolein selectivity remained unimpaired. Catalysts characterization proved that active and selective sites are weak or moderately Brønsted acid sites due to interaction of polymeric niobium oxide species and zirconia support. They also reported the effect of the reaction temperature and the diluting gas flow rate on the catalytic properties of the catalysts. They found that a simple treatment with flowing air at a higher temperature than the reaction temperature can be sufficient to completely regenerate the deactivated catalysts back to their original level of activity.

In another study, Lauriol-Garbay et al. [141] applied acid-base properties of fresh and used niobium–zirconium mixed oxide catalysts ($\text{Zr}_7\text{Nb}_2\text{O}_{19}$, $\text{NbO}_x\text{-}0.3/\text{ZrO}_2$, $\text{NbO}_x\text{-}0.6/\text{ZrO}_2$, m-ZrO₂, t-ZrO₂) for dehydration of glycerol to acrolein. They used various techniques for catalyst characterization such as NH_3 -TPD, infrared spectroscopy of absorbed pyridine, and adsorption microcalorimetry of ammonia and sulfur dioxide. They also studied the relationships between the catalytic properties and the acid-base properties of fresh catalysts. Zirconia support with better niobium oxide species covering (ZrNbO) was the most efficient catalysts with 72% acrolein selectivity and 98% glycerol conversion at 573 K [141]. No specific relationship was reported between the acid-base and selectivity to acrolein. Characterization of used catalysts revealed that the acidic properties had changed noticeably with respect to time. No further strong acid sites were observed and only weak or very weak acid sites were detected. They also introduced a linear relationship between the total quantity of remaining acidic sites and the glycerol conversion rate. The merit of the linear relationship was to take into account an intrinsic activity of the stronger sites, which was more than 10 times of the weaker sites. The deactivation of the catalysts as a function of time on stream was contributed by the formation of cyclic molecules produced by the secondary reaction of acrolein with resulting by-products from the decomposition of hydroxyacetone, possibly acrolein and glycerol.

In another study, Lauriol-Garbey and co-workers [142] investigated the application of WO_3/ZrO_2 catalysts doped with SiO_2 for

glycerol dehydration to acrolein at 573 K. The catalyst was prepared from polymeric WO_x species covering tetragonal ZrO_2 with highly dispersed SiO_2 at the surface that appears to be a key parameter. Various characterization methods revealed that the deposition of SiO_2 on ZrO_2 led to formation of larger meso-porous pores, decreasing the support basicity, and limiting the production of undesired side-product such as coke. The $\text{WO}_x\text{-SiO}_2/\text{ZrO}_2$ catalyst improved the acrolein selectivity from 70% to 78% compared to WO_x/ZrO_2 , with nearly complete glycerol conversion. Furthermore, the catalyst was highly stable as more than 94% conversion was achieved after 100 h reaction time. Various attempts for application of tungsten oxide on zirconia (WO_3/ZrO_2) are summarized in Table 6.

Kim et al. [148] evaluated the application of various silica-alumina catalysts (SiO_2 , $\text{Si}_{0.95}\text{Al}_{0.05}\text{O}_x$, $\text{Si}_{0.9}\text{Al}_{0.1}\text{O}_x$, $\text{Si}_{0.8}\text{Al}_{0.2}\text{O}_x$, $\text{Si}_{0.6}\text{Al}_{0.4}\text{O}_x$, $\text{Si}_{0.4}\text{Al}_{0.6}\text{O}_x$, $\text{Si}_{0.2}\text{Al}_{0.8}\text{O}_x$, $\eta\text{-Al}_2\text{O}_3$) with different Si/Al ratios in gas-phase glycerol dehydration. $\text{Si}_{0.8}\text{Al}_{0.2}\text{O}_x$ illustrated the highest (49.4%) acrolein yield within the first 2 h of reaction time with optimal reaction conditions being 76.3% water content, 23.4 molar flow rate, 0.3 g catalyst weight, and 20.7 h^{-1} WHSV. The order for initial acrolein yield over different catalysts is as follows: $\text{Si}_{0.8}\text{Al}_{0.2}\text{O}_x > \text{Si}_{0.6}\text{Al}_{0.4}\text{O}_x > \text{Si}_{0.9}\text{Al}_{0.1}\text{O}_x > \text{Si}_{0.4}\text{Al}_{0.6}\text{O}_x > \text{Si}_{0.95}\text{Al}_{0.05}\text{O}_x > \text{Si}_{0.2}\text{Al}_{0.8}\text{O}_x > \text{-Al}_2\text{O}_3$. The 1-hydroxyacetone selectivity and acrolein yield highly depended on the Lewis and Bronsted acidic sites, respectively.

Ulgen and Hoelderich [149] obtained a maximum of 85% acrolein selectivity at nearly complete glycerol conversion using WO_3/TiO_2 catalysts in a continuous flow fixed-bed reactor. They discovered that the use of oxygen could stop side products formation. They also studied the effect of reaction temperature, WO_3 loading, carrier used and oxygen on reaction conversion. The main advantage of titania is that it is cheaper than other catalysts such as WO_3/ZrO_2 and pure HPAs. The correlation between catalytic performance and characteristics of the titania carrier revealed that higher acrolein selectivity is produced by enhancing the sulfate content. Indeed, tungsten oxide supported by titania is a very good catalyst for glycerol dehydration due to the slower deactivation rate and cheaper price. However, longer reaction time compared to other catalysts is its main disadvantage.

Cavani et al. [150] used sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) catalyst in gas phase dehydration of crude glycerol to acrolein in the presence of oxygen co-feeding. The highest acrolein selectivity of 42% at 49% glycerol conversion was obtained at optimum conditions being 603 K reaction temperature, 0.25 g catalyst weight, and glycerol/water/oxygen/helium feed ratio of 2/4/40/54. However, the acrolein production was limited by acetaldehyde and heavy compounds products due to mass-transfer limitation condition.

Omata et al. [143] investigated the hydrothermal synthesis of complex metal oxide (W–Nb–O) catalysts for gas phase dehydration of glycerol to acrolein in 3 calcination temperatures (673, 973, and 1273 K). These types of catalysts have a layered structure (linear arrangement of corner-shared octahedral) in the C-direction and a disordered structure in the a–b plane. They could obtain 70.1% and 74.4% acrolein yield with nearly full glycerol

Table 6

Various application of tungsten oxide on zirconia.

T (K)	Cat (wt%)	Y_{AC} (%)	Notes	Ref
573	9	74	–	[143]
563	–	77–79	Oxygen post treatment could regenerate the initial catalytic properties at 623 K for 5 h.	[144,145]
553	19	57	The acidity of catalyst enhanced by increasing the tungsten oxide amount.	[146]
553	–	84.2 [76.3] ^a	Effect of pore condensation evaluated. Nitrogen as a carrier gas showed better result compared to hydrogen. Catalyst was highly stable even after 480 h.	[147]

^a Number in bracket related to acrolein yield with hydrogen flow.

conversion for W–Nb–O catalyst at calcination temperatures of 973 and 673 K, respectively. The main advantages of W–Nb–O catalyst are higher acrolein yield and lower deactivation rate compared to other catalysts such as WO_3/ZrO_2 and HZSM-5. Moreover, researchers tested the acid-treated catalyst (Cs–W–Nb–O) and it exhibited approximately similar acrolein selectivity with W–Nb–O catalyst calcined at a lower temperature (973 K). They concluded that the structure of a–b plane affected the product distribution.

In addition, Chieregato et al. [151] utilized W–Nb–O and W–V–Nb–O catalyst with hexagonal structure in one-pot oxi/dehydration of glycerol to acrylic acid with acrolein as the intermediate. The results indicated that only 1% acrylic acid and 67% acrolein selectivity were obtained over W–Nb–O catalyst compared to 34% acrylic acid and 18% acrolein selectivity by W–V–Nb–O catalyst.

Liu et al. [152] used CrAlPO, CuCrAlPO, and LaCuCrAlPO catalysts for dehydration of glycerol to acrolein in a fixed-bed reactor at 443 K. The results indicated that the CrAlPO showed the lowest glycerol conversion. However, the CuCrAlPO illustrated better results due to the presence of Cu and Cr that have important roles in formation of hydroxyacetone and acrolein, respectively. The meso-LaCuCrAlPO catalyst exhibited the highest acrolein selectivity of 80% and 99% glycerol conversion at 613 K and atmospheric pressure.

Choi et al. [153] developed a new heterogeneous solid catalyst NbPsi-0.5 for glycerol dehydration to acrolein at 523 K. The long-life stability of NbPsi-0.5 catalyst versus HZSM-5, NbPsi-1, and NbP catalysts was evaluated. NbPsi-0.5 acidity is closed to pure Bronsted acid. This catalyst has a well-developed mesoporous structure due to high surface area and large pores. The final acrolein yield for NbPsi-0.5 and HZSM-5 were 76.3% and 76.6%, respectively. However, NbPsi-0.5 displayed only 4.55 mg/mmol coke formation in contrast with HZSM-5 with 5.75 mg/mmol of coke. The NbPsi-0.5 exhibited three times longer stability than other catalysts. These significant results obtained by NbPsi-0.5 may be attributed to the following reasons: (1) catalyst has nearly pure Bronsted acidity, (2) unique structure of catalyst with large meso-pores decreased the possibility of pore blockage by coke, and (3) amount of coking and oxidation temperature reduced.

Massa et al. [154] used niobium and tungsten oxide supported on monoclinic zirconia for gas phase dehydration of glycerol at 573 K reaction temperature. Both catalysts showed reasonable results but tungsten oxide supported by zirconia (0.5 WZr) was slightly better than niobium supported zirconia (1NbZr) catalyst with 78% and 75% acrolein yield at 100% glycerol conversion, respectively. Effect of oxygen co-feeding was also examined in this research. Oxygen had no serious effect on acrolein yield but the deactivation rate of catalyst decreased and also air flow could regenerate the catalyst effectively. HRTEM and XPS revealed that coke and high boiling point compound were the main reasons for catalyst deactivation.

Dar et al. [155] investigated glycerol dehydration to acrolein in a gas-phase over copper catalyst supported by cerium (Ce), zirconia (Zr), and silica (Si) nitrates. Copper supported on zirconium (Cu/Zr) catalyst gave better results with 56.9% acrolein selectivity at 70% glycerol conversion. Hydroxypropanone with selectivity in the range of 11.9–13.9% was the main reaction by product.

Gu et al. [156] used various supported nickel sulfate (NiSO_4) catalysts for gas-phase dehydration of glycerol at 613 K. It was discovered that 17NiSO₄-623 catalyst with lower calcination temperature (623 K) and moderate concentration (17%) was the best catalyst with almost 70 mol% acrolein selectivity and > 90% glycerol conversion during 10 h reaction time. They also evaluated the effect of oxygen and nitrogen co-feeding on the catalyst activity and deactivation process. Oxygen could not improve the acrolein selectivity but it reduced the deactivation rate of the

catalyst. Both sulfate groups and nickel cations showed oxidizability in reaction and the main reason for deactivation of catalyst was loss of sulfur.

Tao et al. [157] investigated application of tantalum oxide ($\text{Ta}_2\text{O}_5\text{-T}$) catalyst, calcined in various temperatures ($T=383\text{--}973\text{ K}$), for dehydration of glycerol at 588 K. The $\text{Ta}_2\text{O}_5\text{-350}$ sample exhibited maximum strong acidity in a range of $-8.2 < H_0 \leq -3.0$ with no basicity. The highest acrolein selectivity (75%) and glycerol conversion (40%) were obtained over $\text{Ta}_2\text{O}_5\text{-350}$ catalyst at 623 K reaction temperature and 0.82 g catalyst weight. The 1-Hydroxyacetone was the main byproduct of this reaction. More importantly, this catalyst exhibited remarkable long-life stability since it remained stable for at least 100 h on stream. Table 7 summarizes recent studies related to the application of different metal oxide catalyst in glycerol dehydration to acrolein.

In contrast with other catalysts such as supported heteropoly acids and zeolites the mixed metal oxides, and phosphates catalysts seem to have less straightforward control of physical properties. The highest ever reported acrolein yield for metal oxides catalysts is 92.6 % at 100% glycerol conversion over $\text{Fe}_x(\text{PO}_4)_y$ catalyst and it could be stable for 25 h. Generally, metal oxide catalysts contain higher Lewis acidic and even basic sites (amphoteric oxides) compared to other groups of catalysts. Therefore, these types of catalysts are less selective to acrolein [12].

3.2. Liquid phase dehydration of glycerol to acrolein

Dehydration of glycerol in the liquid phase was initiated at 1934 by Shell Company [166]. The process used sulfuric acid as catalyst for dehydration of glycerol aqueous solution at 463 K. They obtained approximately 50% acrolein yield. Later, Hoyt and Mannien [167] patented liquid phase glycerol dehydration over a heterogeneous catalyst phosphorous acid supported on clay. More importantly, they used petroleum oil as a reaction medium due to its high boiling point (573 K). As a consequence of the high boiling point of reaction medium and application of heterogeneous catalyst, they obtained 72.3% acrolein yield. However, the liquid glycerol dehydration similar to gas phase process remained undeveloped till cheaper glycerol source became available in the last decade.

Recently, supercritical water reforming (SCWR) of glycerol with or without catalyst attracted much attention for value-added chemicals production, mainly acrolein [168]. Ramayya et al. [169] used homogeneous catalyst (H_2SO_4) in a batch type reactor at reaction conditions near to supercritical water ($P=22.1\text{ MPa}$ and $T=657\text{ K}$). The highest acrolein selectivity of 86% at 55% glycerol conversion was obtained at optimal condition of 623 K reaction temperature and 34.5 MPa pressure, and 5 mmol catalyst. The main advantage of this process was its physical characteristics such as the ion product and dielectric constant. However, the application of homogeneous catalyst and batch type reactor was the main weak point of this process due to the additional catalyst separation process in the downstream and cumbersome batch reactor for industrial application.

Buhler et al. [170] investigated the application of supercritical water method in a continuous reaction system without any catalyst. They obtained different products such as formaldehyde, acetaldehyde, propionaldehyde, allylic alcohol, and acrolein. However, the yield of acrolein was only in the range of 10–27% at the optimum condition being 623 K temperature and 45 MPa pressure. They concluded that the main reason for low acrolein yield was catalyst absence. Watanabe et al. [29] used similar reaction conditions and supercritical water method of Buhler et al. [170] except they used continuous flow reactor instead of batch one. The acrolein yield improved to 74% at 92% glycerol conversion.

Table 7

Recent applications of metal oxide catalysts in dehydration of glycerol to acrolein.

Prepared catalyst	Best catalyst	T (K)	TOS	Con (%)	S _{AC} (%)	Y _{AC} (%)	Reason for catalyst activity	Ref
15%WO ₃ -Zr (CP)	15%WO ₃ -Zr (CP)	588	2	77	71	–	Pt and Pd improved catalyst stability with O ₂ co-feeding and the Y _{AC} > 62% for 30 h at 93% Gl conversion.	[158]
15%WO ₃ -Zr (AN) (Na, K, Ag, Ni, Pt, Pd, and Rh)								
5–30% VPO-Zr	20%VPO-Zr	573	5	100	66	–	Total acidity and Bronsted acidic site	[159]
–	Industrial ZR24	543	–	94	82	–	A new reaction mechanism proposed	[160]
8–40%WO ₃ -Al calc at 700–900 °C	30%W-Z-800	588	10	90	69	–	The 3.5–7.6 W nm ^{−2} surface density of W atoms caused higher AC selectivity, either on Al and Zr.	[161]
9–23%WO ₃ -Al calc at 650 °C								
5–40%WO ₃ -Z calc at 550–900 °C								
WO ₃ & V ₂ O ₅	WO ₃ & W ₁ V _{0.25}	573	–	100	–	50.3	Catalysts used for two-steps oxi-dehydration of glycerol to acrylic acid. W ₁ V _{0.25} catalyst reached to 25.7% acrylic acid yield.	[162]
W ₁ -V(0.25–4)								
MO ₁ -V(0.25–4)								
G1: CeO ₂ & MgO; G2: ZrO ₂ & Nb ₂ O ₅ -700; G3: Al ₂ O ₃ , HZSM-5,	MgO	588	10	13	20	–	Mixture of 10% 1,2-PD or 1,3-PD with glycerol used as feedstock. The solution of glycerol and 1,3-PD could produce acrolein even with low selectivity (1–22%).	[163]
15%WO ₃ /ZrO ₂ , 5%H ₃ PO ₄ /αAl ₂ O ₃ , SAPO-34; G4: SiO ₂ -Al ₂ O ₃ , H β , Nb ₂ O ₅ -350 (2.3–4.3)W-(0.5–6.7Si)/ZrO ₂ -E (2.5–4.1)W-ZrO ₂ 2W/ZrSiO ₂ -SG	SiO ₂ -Al ₂ O ₃			47	20	–		
	H β			12	22	–		
	3.8W0.95Si-ZrO ₂ -E	573	20	100	80	–	Catalyst could remained stable for 140 h with S _{AC} > 70. Besides, 3.5W6.7Si-ZrO ₂ -E and 2.5W/ZrO ₂ -A showed similar results with slightly S _{AC} < 70%.	[164]
H ₂ SO ₄ treated Zr/HMS Pre-sulfated Zr-Al/HMS Chlorosulfonic acid treat Zr/HMS W-Zr-Al/HMS (0.25–0.75)Nb(0.25–0.75)W-Al (0.25–0.75)Nb-(0.25–0.75)W-Si (0.25–0.75)Nb-(0.25–0.75)W-Ti 1Nb-Al, Ti, Si; 1W-Ti, Al, Si	W-Zr-Al/HMS	528	10	86	60	–	Moderate Lewis acidic site. Reducibility up to 6 times.	[114]
	0.5Nb0.5W-Al	578	3	100	71.9	–	Bronsted and Lewis acidic sites. 0.5Nb0.5W-Al reached to S _{AC} =71.9% without O ₂ co-feeding, but, 1WTi obtained S _{AC} =80% with O ₂ co-feeding.	[165]
	1W-Ti				80			

Ott et al. [171] evaluated the effect of supercritical water condition as a reaction medium in a continuous high pressure tubular reactor in the presence of heterogeneous zinc sulfate (Zn-SO₄) catalyst. Water is highly corrosive in its supercritical conditions and the addition of strong acid to this reaction medium enhanced corrosion. Therefore, the reactor required expensive and particular steel grade to be protected from corrosion. It was the main reason that researchers chose ZnSO₄ as a catalyst since it was not a strong acid for liquid phase dehydration of glycerol. The highest acrolein selectivity of 75 mol% with 50% glycerol conversion obtained at 633 K reaction temperature, 25 MPa pressure, and 470 ppm (gg^{−1}) ZnSO₄ catalyst amount. Furthermore, they focused on kinetic analysis of this reaction which followed the first-order reaction rate with 140 ± 12 kJ/mol activation energy and 1.3×10^8 s^{−1} frequency factor. The reaction rate constants at various temperatures and pressures are summarized in Table 8. Similarly, Lehr et al. [172] used supercritical water condition for liquid dehydration of polyols (m-erythritol, glycerol, 1,2-, 1,3-propanediol, and 1,2-butanediol) that were derived from sugars by hydrogenolytic cleavage or biochemical conversion. They reported 60% acrolein selectivity at 59% glycerol conversion in supercritical water condition.

Suzuki et al. [173] and Yoshimi et al. [174] investigated liquid phase glycerol dehydration at high reaction temperature under atmospheric pressure. They used potassium bisulfate (KHSO₄), magnesium sulfate (MgSO₄), and phosphorous alumina (5 wt% H₃PO₄/Al₂O₃) catalysts at 553 K reaction temperature and atmospheric (0.1 MPa) reaction pressure with paraffin as a reaction solvent medium. The MgSO₄ and H₃PO₄/Al₂O₃ catalysts registered low acrolein yields of 52% and 51%, respectively at nearly 90% glycerol conversion. However, potassium bisulfate (KHSO₄) exhibited 80% yield for acrolein at 97% glycerol conversion. These researches were continued by Takanori et al. [175,176] who utilized copper (CuPO₄) or iron (FePO₄) phosphates as heterogeneous catalysts with high boiling reaction mediums such as m-xylene, n-octane, and sulfolane. They obtained 84% acrolein

Table 8
Reaction rate constants of glycerol dehydration over zinc sulfate [171].

Pressure (MPa)	Temperature (K)	k/s ^{−1}	R ²
25	573	0.0010 ± 0.0002	0.92
25	603	0.0053 ± 0.0005	0.90
25	633	0.0161 ± 0.0011	0.97
28	633	0.0208 ± 0.0020	0.97
31	633	0.0249 ± 0.0019	0.98
34	633	0.0255 ± 0.0027	0.97

yield at near complete (98%) glycerol conversion in the presence of CuPO₄ at 553 K.

De Oliveira et al. [177] investigated the liquid phase glycerol dehydration to acrolein over various catalysts such as H β , HY, Mordenite, ZSM-23, SBA-15, HY/CVD, Pt/HY, and Pt/SBA-15. The HY catalyst exhibited the highest acrolein selectivity of 99.5% at 89% glycerol conversion. In contrast, SBA-15 produced 84% acrolein selectivity at only 40.6% glycerol conversion which was the lowest among different catalysts in this research. The modification process by Pt and CVD could not improve the selectivity and conversions of this reaction, but surprisingly the acrolein production decreased due to destruction of external acidic sites and agglomeration of metals. SBA-15 and HY demonstrated the highest deactivation by acid site poisoning possibly due to catalyst pore blockage by heavy glycerol derivatives.

Recently, Shen et al. [178] have tested the catalytic activities of silicotungstic (HSiW), phosphotungstic (HPW), and phosphomolybdic (HPMo) acids in the liquid phase dehydration of glycerol to acrolein in a semi-batch reactor. They also studied the influence of HPAs acidities on the glycerol conversion and the products yield. The catalysts activities toward the acrolein production were in the order of HSiW > HPW > HPMo. Therefore, the highest yield of acrolein (78.6%) was achieved by silicotungstic acid catalyst at 573 K with 1:0.0001 glycerol/catalyst molar ratio. The main by-products of this reaction were acetic acid and hydroxyacetone

with lower than 10% yield. Researchers concluded that this process is a potentially practical method due to the low energy demand, less catalyst consumption, and high acrolein yield.

Calvino-Casida et al. [179] for the first time used microwave irradiation for acrylonitrile production from glycerol without any solvent in liquid phase. The group reported acrolein as the main product with 85% selectivity and 38% glycerol conversion at 373 K reaction temperature after 1 h in the absence of any catalyst. They concluded that microwave irradiation initially transformed glycerol to acrolein and rutile VSbO₄ was efficient for carbon-nitrogen bonds reaction for conversion of acrolein to acrylonitrile.

Yang et al. [180] synthesized super-acid sulfated zirconia (ZrO₂/SO₄²⁻) supported on mesoporous silica (Szs) for dehydration of glycerol in liquid phase. In addition, application of AlCl₃ and HPW catalysts were evaluated in this study. The results indicated the highest acrolein yield of 16.73% and 11.24%, for sulfated zirconia and HPW respectively. However, the prepared SzS catalyst showed considerable activity of 9.87% acrolein yield. Easy separation of SzS catalyst from the product is the main advantage of this catalyst.

Antal et al. [181] used NaHSO₄ catalyst in super-critical water (SCW) condition (35 MPa and 633–773 K) for decomposition of glycerol and cellulose. They demonstrated that at higher temperature (773 K) formation of H₂, CO, and CO₂ was favoured for reaction due to the presence of free radical mechanism that caused carbon–carbon cleavages. However, lower temperature heterolytic reaction involving ionic intermediates led to acrolein production. Krammer et al. [182] reported that hydrolysis, hydration, and dehydration reactions performed at SCW conditions in the absence of catalyst could produce high yield and selectivity of desired products such as acrolein from glycerol at 623 K reaction temperature and 25 MPa pressure.

Qadariyah et al. [183] produced acrolein, acetaldehyde, and allyl alcohol from glycerol in SCW condition of 473–673 K reaction temperature and 30 MPa pressure in 20–180 min reaction time. They reported that acetaldehyde was produced only in sub-critical water condition, but allyl alcohol was formed in supercritical condition and acrolein was identified in both sub- and super-critical conditions. Changing in the reaction pathways (from ionic to free radical) was the main reason for the product distribution.

Akizuki and Oshima [184] used TiO₂ and WO₃/TiO₂ catalysts for dehydration of glycerol in SCW condition at 673 K reaction temperature and 33 MPa pressure. The results indicated that increasing WO₃ concentration in catalyst improved glycerol conversion and also acrolein yield. They also proposed first and pseudo-first order reaction rate for this reaction.

Shen et al. [185] reported application of Bronsted acidic ionic liquid (BAIL) catalysts ([Hmim], [N₂₂₂₄], [Bmim], [BPy], [PsPy] supported with HSO₄ and H₂PO₄) in glycerol dehydration to acrolein using semi-batch process. The [Bmim]H₂PO₄ and [Bmim]HSO₄ catalysts gave the highest acrolein yield of 57.4% and 50.8%, respectively with 100% glycerol conversion at 543 K reaction temperature and 1:100 molar ratio of catalyst to glycerol. The [Bmim] cations of Bronsted acidic ionic liquid and moderate

acidity of catalyst were the main reasons for higher acrolein production in this liquid phase process. Table 9 summarizes recent attempts for glycerol dehydration to acrolein in liquid phase.

According to the recent literatures and researches, the application of high boiling point liquids as reaction medium at atmospheric pressure is more suitable for liquid phase dehydration of glycerol. However, the main obstacle for this process at industry or commercial level is the adaption of the laboratory scale process to the large scale plant. Apart from the engineering aspect, the process also requires high investment and maintenance costs. Thus, this process still needs further investigations to overcome all drawbacks for industrialization.

3.3. Physico-chemical effect of catalyst on acrolein yield

3.3.1. Catalyst acidity

Acidity of catalyst has significant effect on the catalytic activity and stability. Dubois et al. [116,190], for the first time, evaluated the influence of acidity for various catalysts such as heteropoly acids, zeolites, different metal oxides, and Nafion on acrolein selectivity. The zirconium and tungsten oxides have HA = -14.5 and Nafion has HA = -12. These catalysts achieved up to 70% acrolein selectivity at 100% glycerol conversion although the zeolite catalysts with HA < +2 exhibited only 60% selectivity for acrolein. Thus, catalysts with HA in the range of -10 to -16 were the better choice for dehydration of glycerol to acrolein.

Chai et al. [96–97] focused on effects of acidity by application of various acid catalysts and niobium oxides. The results indicated that calcination temperature had significant effect on the catalyst acidity. The highest 50% acrolein selectivity at 90% glycerol conversion was obtained at low calcination temperature (523–573 K). These catalysts also exhibited larger specific surface area compared to ones that were calcined at higher temperatures. Nonetheless, these types of catalysts deactivated rapidly. Therefore, authors concluded that the strength of acidity should be carefully controlled and fine-tuned since too strong acidity caused quick deactivation while too weak acidity produced low acrolein selectivity. A summary of Chai et al. [97] evaluation on the acidity of a large number of catalysts for acrolein production is provided in Table 10.

The type of acidic sites (Bronsted and Lewis acids) on the surface of catalysts has significant effect on catalytic activity. Alhanash et al. [101] studied the application of pure Lewis acid catalyst (tin-chromium mixed oxide) versus pure Bronsted acid catalysts (acid cesium salts of phosphotungstic). They concluded that the Lewis acid catalysts required higher reaction temperature since the catalysts have larger activation energy (E_a) compared with the Bronsted acid types. In addition, Lewis acid catalysts produced higher acetol selectivity which is the main by-product for glycerol dehydration. Kim et al. [119] also reported similar results for the application of HZSM-5 with various ratios of Si/Al. Suprun et al. [131] evaluated the textural and acidity effect of

Table 9
Recent studies in liquid phase dehydration of glycerol to acrolein.

Prepared catalyst	Best catalyst	T (K)	TOS	Con (%)	S _{AC} (%)	Y _{AC} (%)	Reason for catalyst activity	Ref
10–50%PO ₄ –Nb ₂ O ₅	50%PO ₄ –Nb ₂ O ₅	513	2	68.1	72	–	Higher surface acidity by increasing amount of PO ₄ support	[186]
MgAl-LDH	MgAl-LDH (500)	513	2	52.6	15.2	–	Calcined catalysts were favorable for acetol production with 82.1% selectivity.	[187]
NiMgAl-LDH Calc at 400–600 °C								
HNa-β-(0–4) H-MFI	HNa-β-4	473	–	32	57.8	18.5	Higher Na ⁺ /H ⁺ ratio increased selectivity of acrolein but decrease conversion. Similarly, smaller pores reduce catalyst activity but increase acrolein selectivity.	[188]
(0–100%) Nano Cu-ZSM-5	8%Cu/ZSM-5	523	2	100	91.2	91.2	–	[189]

Table 10

Various acidity groups and effect of them on acrolein production [97].

Catalyst type	HA range	Results
Group 1 Basic catalyst (magnesium oxide)	> +7	No acrolein selectivity
Group 2 Zirconium oxide	-3 ≤ HA ≤ +7	High acrolein selectivity [92], but not more than 30%, stable for 10 h
Group 3 Alumina supported phosphorous acid, alumina supported heteropoly acid, niobium oxide, HZSM zeolite, pure alumina	-8 ≤ HA ≤ -3	High selectivity of acrolein (70% for supported HPA, tungsten oxide/zirconium oxide), low stability and rapid deactivation
Group 4 H β , niobium oxide (calcined at 623 K), alumina-silicate, sulfonated zirconium oxide	HA ≤ -8	Less selectivity than group 3. But, more stable than those on stream

various catalysts such as phosphate-modified titania, alumina, and silica/alumina (SAPO) on acrolein selectivity. They reported that the higher acidic catalyst (silica–alumina phosphate (SAPO)) exhibited higher acrolein selectivity of 72% at 553 K. In addition, they concluded that micro-porous material (5–6 Å) had low activity because of their interval diffusion limitations which enhanced the coke formation.

De Oliveira et al. [178] evaluated the effect of acidity, structure, and textural characteristics of various catalysts in liquid phase dehydration of glycerol to acrolein. Lower Si/Al ratio and larger pore volume such as HY showed the highest acrolein selectivity (99.5%). In contrast, SBA-15 catalyst with weak acidity gave lower acrolein selectivity of 84%. They reported that catalysts activity had a similar order as their acidity (HY > H β > Mor > SBA-15 > ZSM-23). The blockage of pores was the main reason for catalyst deactivation while acid site poisoning was less important. In addition, small pore size such as Mordenite and ZSM-23 had weak to strong acid sites. However, the main reason for their deactivation by coking was one-dimensional structure of their channels. Nevertheless, mesoporous SBA-15 with mild acidity could produce reasonable acrolein selectivity at 84%.

Stosic et al. [191] synthesized a series of calcium phosphate compound catalysts (1.5HAP, 1.66HAP, Ca/HAP, P/HAP, W/HAP) with different Ca/P ratios and also impregnated hydroxyapatite (HAP) with tungsten oxide. Gas phase dehydration of glycerol was conducted at 623 K in a fixed-bed pyrex reactor. They also studied the structural, textural, and surface properties of prepared catalysts. It was shown that the Ca/P ratio, in addition to influence on acidic/basic features, also can affect redox properties of the catalysts. The application of bi-functional catalysts allowed the substrate to react with both basic and acidic sites, thus undergoing competitive reactions. The study indicated, since maximum acrolein selectivity depended on active acid sites, it is essential to increase acidity and also hinder base sites. Moreover, glycerol can react through a complex reaction network with numerous consecutive and side reactions. This study also proved that reducing strength and number of acid centers can enhance the acetol yield.

3.3.2. Textural properties (pore size)

The research by Tsukuda et al. [192] discussed about the effect of catalyst textural properties (pore size) on acrolein yield. They used various heteropoly acids (phosphotungstic acid ($H_3PW_{12}O_{40}$), silicotungstic acid ($H_4SiW_{12}O_{40}$), and molybdenum base homologous acid ($H_3PMo_{12}O_{40}$)) as based catalysts and different sizes (3, 6, and 10 nm) of the meso-pores on silica support. Acrolein selectivities of 74% and 65% at complete glycerol conversion were obtained by $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, respectively over the 6 nm average pore diameter silica support. However, the silicotungstic ($H_4SiW_{12}O_{40}$) catalyst supported by 10 nm pore diameter of silica produced up to 86% acrolein selectivity. In contrast, smaller (3 nm) silica supports reduced the selectivity to 67% at only 55% glycerol conversion and enhanced coke formation.

Besides, Atia et al. [193] used silicotungstic acid ($H_4SiW_{12}O_{40}$) with alumina support (5 and 12 nm pore size) in a similar reaction condition studied by Tsukuda et al. [192]. They reported 65% and 85% acrolein selectivity for 5 nm and 12 nm pore size, respectively, with 100% glycerol conversion at 548 K.

According to the results of the latter study, the active phase dispersion and the pore size of the support phase have significant effect on the catalytic activity. Therefore, different researchers such as Xu et al. [194], Sato et al. [195], and Jo et al. [196] focused on these parameters in gas phase dehydration of glycerol to acrolein with supported HPAs. The results indicated that silicotungstic acid ($H_4SiW_{12}O_{40}$) catalyst supported on silica with pore diameter sizes of 6 and 10 nm could produce 87% acrolein selectivity at 548 K. However, the 3 nm pore size catalysts and 573 K reaction temperature caused reduction in catalyst performance. Pathak et al. [146] evaluated the influence of ZSM-5 catalyst pore size (0.54, 0.74, 3.15, and 11.2 nm) on acrolein selectivity. Finally, they concluded that the selectivity surged with pore size, although, the selectivity of other by-products such as acetol, formaldehyde, and acetaldehyde reduced at the same time.

Temperature treatment is highly positive approach for modification of textural properties of catalyst. This method forms larger pore size and decreases the specific surface areas. In fact, temperature treatment prevents acetol formation and slows down the catalyst deactivation process.

Gu et al. [197] studied a series of H-zeolite catalysts (HZSM-5, H β , HY, HZSM-11, nano HZSM-5, and nano HZSM-11) to investigate the effect of the channel structure on catalytic performance in gas phase dehydration of glycerol to acrolein. They reported HZSM-5 catalysts can exhibit better performance compared to H-Beta and HY. H-zeolites were preferable for reactions requiring smaller channels that are marginally larger than the molecular diameter of glycerol. Various characterization tests revealed that the total acid amount increases in the following order: HZSM-11 < nano HZSM-5 ≈ nano HZSM-11 < bulk HZSM-5 < H-Beta < HY. Nano-sized HZSM-5 and HZSM-11 exhibited highest catalytic performances in this study due to its smaller channels that enhance diffusion. The highest acrolein selectivity of 74.9 mol% and 81.6 mol% glycerol conversion was achieved over nano HZSM-11 (300–500 nm) at 8 h reaction time.

There are some key factors for better acrolein production over H-zeolites such as particle size and small channel diameter. It was also observed that two kinds of coke were formed during the reaction graphite-like layered coke deposited on external surface of H zeolites and oxygen-containing alkylated mono- or bi-aromatics or oligomers trapped at intersections of the channels. In addition, the Bronsted acid sites in channels or channels intersections were responsible for glycerol dehydration.

3.4. Catalyst deactivation and regeneration

Aforementioned researches have discovered a wide variety of catalysts for dehydration of glycerol to acrolein. However, the main

obstacle for industrial application of these catalysts is rapid deactivation due to coke formation on the catalyst surface. Erfle et al. [102] and Suprun et al. [131] reported that the Bronsted acid sites or generally acid sites are responsible for coke formation. Furthermore, higher reaction temperature and smaller catalyst pore size enhanced the amount of coke formed. Table 11 summarizes the experimental results by different catalysts. Some researchers proposed three main solutions to slow down the catalyst deactivation as listed in Table 12.

Dubois et al. [116] initiated the method of co-feeding with air in glycerol dehydration to acrolein over zeolite catalysts (β -zeolite and HZSM-5). The main challenge in this process was that high oxygen fraction ($> 7\%$) may lead to explosion. Thus, they used different ratios of 6%, 4.5%, and 82.5%, for oxygen, glycerol, and steam feed, respectively. The amount of oxygen co-feeding could reduce catalyst deactivation and prevent the formation of acetol as a by-product in this process. However, the acrolein selectivity remained constant even with oxygen co-feeding. Oxygen co-feeding was also performed by other researchers over various catalysts such as vanadium pyrophosphate (VPO-800) [132], boron phosphates (BPO) [134], iron phosphates ($\text{Fe}_x(\text{PO}_4)_y$) [149], tungsten oxide on zirconia (19 wt% WO_3/ZrO_3) [199], and cesium salts of phosphotungstic acid (CsPW) [200]. The studies are summarized in Table 13.

According to the results of these researches, oxygen co-feeding had little influence on acrolein selectivity over vanadium pyrophosphate (VPO-800) and tungsten oxide on zirconia (19 wt% WO_3/ZrO_3) catalysts and only 5% oxygen flow enhanced the selectivity of acrolein. However, in this method the acrolein selectivity dramatically decreased over boron phosphate (BPO) and iron phosphate ($\text{Fe}_x(\text{PO}_4)_y$) by 16% and 29%, respectively as the most was oxidized to carbon oxides (CO and CO_2). Interestingly, the only catalyst that was significantly influenced by oxygen co-feeding was cesium salts of phosphotungstic acid (CsPW) which the acrolein selectivity was doubled from 47% to 93%. Furthermore, Kasuga et al. [201] evaluated the application of MFI protonated zeolite catalyst with and without modification by co-feeding with air. In their study, unmodified catalyst only produced 45% acrolein selectivity in 24 h reaction time. The modified catalyst by metals (Pt, Pd, Ru, Cu, Ir, and Au), however, illustrated better results

particularly 0.1 wt% Pt and 1 wt% Au that reached to 80.7% and 79.7% yield of acrolein, respectively in 150 min reaction time.

As mentioned before, the oxygen ratio must be less than 7 mol% to avoid the explosion limits. Therefore, Wang et al. [133] evaluated the effect of high and low oxygen concentrations on catalytic activity of vanadium phosphate (VPO). They reported that both very high and low oxygen concentrations reduced the acrolein selectivity. High oxygen concentration enhanced the selectivity of acetic acid, carbon dioxides, acetaldehyde, and acrylic acid. However, low oxygen concentration induced larger amounts of acetol.

Other researchers have used hydrogen (H_2) and sulfur oxide (SO_2) co-feeding for regeneration of used catalyst. Alhanash et al. [101] utilized H_2 co-feeding to regenerate cesium salts of heteropoly acids (0.5% Pd–CsPW) doped by some noble metals (ruthe- nium (Ru), palladium (Pd), and platinum (Pt)). Surprisingly, this process had no effect on acrolein selectivity and even decreased it by 2%. Only the glycerol conversion was improved from 41% to 79% in 5 h. In another study, Dubois et al. [200] injected 250 ppm sulfur dioxide (SO_2) as a co-feed to inhibit catalyst deactivation. Similar to H_2 injection, the SO_2 co-feeding also could not improve the acrolein selectivity. However, glycerol conversion improved from 69% to 87% for 24 h on-stream dehydration reaction. Moreover, SO_2 co-feeding dramatically reduced the acetol formation from 2.4% to only 0.2%. Toxicity was the main drawback of this feeding process.

Another approach for catalyst regeneration is periodic regeneration that was applied by Arita et al. [202] who utilized HZSM-5 as catalyst with air co-feeding. The results demonstrated that initial performances of catalyst can be recovered by this method. Nonetheless, the regeneration exothermicity developed hot-spots in the reactor. Thus, this method can raise the reaction temperature more than 100 °C. Indeed, this process is not suitable for catalysts with temperature sensitivity due to thermal decomposition of catalyst.

In another research, Atia et al. [193] used various HPAs with alumina supports up to 300 h reaction time. Their results indicated that acrolein selectivity remained stable, but the glycerol conversion steadily reduced. They hypothesized formation of coke on the surface of catalyst reduced catalyst activity sites. Researchers used

Table 11
Correlation of acidity and carbon deposit in phosphate catalysts [10].

Catalyst	Ac^{a} ($\mu\text{mol NH}_3 \text{ g}^{-1}$)	D_p^{b} (Å)	$S_{\text{BET}}^{\text{c}}$ (m^2/g)	$T_{\text{reaction}} = 553 \text{ K}$		$T_{\text{reaction}} = 573 \text{ K}$		$T_{\text{reaction}} = 593 \text{ K}$	
				Coke loading (wt%)	H/C ratio	Coke loading (wt%)	H/C ratio	Coke loading (wt%)	H/C ratio
$\text{Al}_2\text{O}_3-\text{PO}_4$	295	111	118	2.4	0.54	3.9	0.52	5.8	0.49
TiO_2-PO_4	258	101	38	3.1	0.55	6.8	0.50	8.9	0.48
SAPO ^d -11	1330	6	172	4.6	0.68	7.4	0.55	9.5	0.40
SAPO-34	498	5	49	9.6	0.62	12.7	0.54	16.2	0.47

^a Total acidity.

^b Pore diameter.

^c Specific surface area.

^d Silica–alumina–phosphate.

Table 12
Three main solutions to slowdown catalyst deactivation.

Method	Main disadvantages	Ref
Co-feeding of hydrogen or oxygen	Explosive condition generation; Oxidation of reaction products	[116]
Cyclic regeneration of used catalyst by oxygen or air flow/pulse injection Moving bed reactor for circulation of catalyst by regeneration in a separate parallel vessel	Loss of productivity The operation and construction of a circulating bed reactor requires serious technological difficulties	[198] [48]

Table 13

Effect of oxygen co-feeding on catalytic performance.

Catalyst	T _{reaction} (K)	Catalyst weight (g)	Co-feed	Time (h)	Conversion (%)	Acrolein selectivity (%)	Acetol selectivity (%)	Yield (%)	STY ^a (mmol/g h)	Ref
VPO-800 ^b	573	0.2	O ₂	nc	100	65	6	65	5.8	[132]
	573	0.2	–	nc	95	60	12	57	5.1	
BPO ^c	553	0.3	O ₂	nc	100	65	8	65	0.8	[134]
	553	0.3	–	nc	96	81	6	78	0.9	
Fe _x (PO ₄) _y	553	1.3	O ₂	5	100	63	0	63	1.7	[149]
	553	0.8	–	5	100	92	0	92	4.1	
19 wt%WO ₃ /ZrO ₃	553	5	O ₂	nc	73	74	8	54	8.9	[199]
	553	5	–	nc	83	69	10	57	9.3	
CsPW ^d	533	23	O ₂	nc	100	93	nc	93	3.0	[200]
	nc	23	–	1	83	47	3	39	0.7	

^a STY: Space-time-yield.^b VPO: Vanadium oxophosphate calcined at 1073 K.^c BPO: boron phosphate.^d CsPW: Cs_{2.5}H_{0.5}PW₁₂O₄₀.

a treatment method of 1% oxygen (O₂) in nitrogen (N₂) co-feeding at 598 K for 24 h to demonstrate their hypothesis. Finally, the regenerated catalyst exhibited fresh catalyst performance.

Innovative reactor design is another approach to slow down catalyst deactivation. A circulating bed reactor, first patented by Dubois et al. [116,190] and adapted by Corma et al. [48] and O'Connor et al. [198] was applied to reduce deactivation rate. Both researchers injected crude glycerol directly to the FCC plant since the required energy for glycerol evaporation can be provided by coke burning. However, they expanded their work for reformation of glycerol to propylene and ethylene at 773–873 K where glycerol was a suitable substitute for naphtha cracking.

Apart from the conventional catalyst regeneration methods that a large number of researchers are currently using, Kasuga et al. [203] used three types of pretreatment methods, including (1) flow of nitrogen, water, and acetol, (2) flow of air, water, and acetol, and (3) flow of nitrogen, water, and acrolein on Alox alumina and protonated MFI zeolite catalysts. The MFI catalysts displayed higher selectivity for acrolein at the initial (150 min) phase which surmised the method is suitable only for early stages of the reaction. Furthermore, Alox gave very low acrolein yield with and without this treatment method.

Cavani et al. [204] studied the catalyst deactivation that occurred during glycerol dehydration in the presence of sulfated zirconia as solid acid catalyst. They synthesized a series of sulfated zirconia catalysts such as SZ0, SZ2, SZ3, and SZ4 with different sulfate amounts at 0, 2.0, 3.8, and 4.4 wt%, respectively and found a close correlation between the sulfate content and catalytic behavior. They reported that the accumulation of carbon residues on the catalyst surface, the self-reduction of sulfuric into sulfurous groups, the leaching of sulfate from catalysts (due to the hydrolysis of sulfate groups) and the formation of volatile esters have major roles on catalyst deactivation. In fact, the catalytic behavior was greatly affected by the amount of sulfate loading into the catalysts.

They concluded that there were two (reversible and irreversible) main causes for catalyst deactivation. The SZ4 sample indicated reversible deactivation due to the reduction of sulfate to sulfite in anaerobic condition which increased the Bronsted acidic site strength. Conversely, the majority of Lewis acid site strength decreased. However, oxygen co-feeding regenerated the main catalytic activity due to re-oxidation of sulfate. Also, oxygen flow led to coke formation and finally deactivated the catalyst (SZ4). The irreversible deactivation of the catalyst was caused by progressive loss of sulfate from the catalyst.

Katryniok et al. [205] used SBA-15, STA/SBA-15, ZrO₂/SBA-15 and STA/ZrO₂/SBA-15 catalysts for glycerol dehydration to acrolein

to evaluate catalyst regeneration by continuous dry or wet air co-feeding and periodic regeneration methods. The results indicated that zirconia-grafted silica as a support for STA dramatically improved the thermal stability of the active catalyst. The acrolein yield reached up to 71% in the first 30 min of reaction and decreased to 37% after 1 h. Both dry and wet air co-feeding could significantly improve the catalytic activity. The methods led to 77–78% acrolein yield. However, the continuous dry or wet co-feeding of air could not regenerate the STA/SBA-15 catalyst and the acrolein yield reduced from 71% in the first 30 min to a range of 30–42% after 6 h of reaction. Besides, both catalysts were utilized under alternating feed short cycles (10 min) of air and glycerol. The zirconia free silica (STA/SBA-15) showed higher acrolein yield due to the absence of an activation period in this case. In fact, the 20 wt% STA on SBA-15 catalyst by application of periodic regeneration methods could exhibit 76% and 74% acrolein yield even after 24–25 h and 96–97 h reaction time, respectively. However, catalyst activity of the 20 wt% STA on ZrO₂/SBA-15 significantly decreased and the acrolein yield reached to only 35% after 24–25 h reaction.

Bronsted acid catalysts led to high acrolein selectivity with short catalyst life-time, but Lewis acid catalysts have longer activation period that enhanced the long-term reaction. Therefore, the regeneration methods have different effect on Bronsted and Lewis acidic sites of catalysts. The Bronsted acid catalyst performed better in a fluidized catalytic bed reactor due to a short contact time in the reaction zone. In contrast, the optimum regeneration process for Lewis acid catalysts is the same as a moving bed process. In fact, if the residence time of catalyst increased to hours or days, the activation period of catalyst seriously decreased.

3.5. Reaction mechanism

Glycerol pyrolysis has been widely studied in gas and liquid phases. The major products are formaldehyde (methanal), acrolein (2-propenal), and acetaldehyde (ethanal) as a result of glycerol fragmentation and dehydration at lower reaction temperatures. Some other products include molecular hydrogen, methane, carbon dioxide, and ethylene in higher reaction temperatures with more complex chemistry. There are some proposed mechanisms for the formation of these products. However, the mechanisms reaction rates, activation energies, and frequency factors for majority of glycerol reactions are still unknown. According to the wide variety of researches in this field, researchers recently focused on

industrialization or commercialization of acrolein production by catalytic dehydration of glycerol. Thus, the identification of the intermediate steps and demonstration of by-products formation are essential.

Buhler et al. [171] proposed the first glycerol dehydration reaction mechanism in the liquid phase with two reaction pathways of a radical or an ionic reaction (Fig. 10). Fig. 10a illustrates the radical mechanism initiated by hydrogen (H_2) abstraction of glycerol that formed a radical. As a result, acrolein formed due to elimination of water and OH^- radical. Acrolein can be produced by other C_3 -radicals minor reaction pathways. In contrast, the ionic mechanism (Fig. 10b) acrolein can be formed as a result of two simple reaction steps of secondary OH-group protonation and secondary carbonium ion formation by H_2O elimination. Similarly, it is possible for primary carbunium ion due to a simple H_2O elimination and deprotonation. However, acetaldehyde and formaldehyde were formed because of the existence of primary carbonium ion competition reaction.

Furthermore, the reaction mechanism of gas phase dehydration of glycerol was firstly proposed by Tsukuda et al. [192]. They demonstrated that controlling the first dehydration step is the key factor for higher acrolein selectivity. In addition, Chai et al. [96] added the reaction pathways of allylic alcohol and 1,2-propanediol to this mechanism (Fig. 11). The glycerol reaction pathways began with dehydration including the terminal $-OH$ (step 1) and central $-OH$ (step 2) that led to two enol intermediate formation. These enols rapidly changed to 1-hydroxyacetone and 3-hydroxypropionaldehyde (3-HPA). The 3-HPA is highly unstable at 588 K reaction temperature and it can be used in the next dehydration for acrolein production (step 3). Also, the unstable 3-HPA decomposed by reversed aldol condensation to formaldehyde and acetaldehyde (step 4). Further

decomposition or hydrogenation of formaldehyde produced carbon oxide (CO), hydrogen (H_2), and methanol (CH_3OH) (steps 5 and 6).

As mentioned before, Chai et al. [96] added the secondary hydrogenation of acrolein to allyl alcohol (step 7) and the hydrogenation of 1-hydroxyacetone carbonyl group to 1,2-propanediol (step 8) by some types of solid base catalyst such as CeO_2 , La_2O_3 , and MgO .

Fig. 12 illustrates the main conversion pathways of glycerol and by-products at a temperature range of 623–773 K. Temperatures beyond 873 K could lead to decarbonylation of acrolein along with other oxygenates to ethylene, other low weight olefins, and carbon monoxide (CO). Eventually, steam cracking of dehydrated species and glycerol could produce H_2 and CO at high temperature, as more H_2 and CO_2 can be produced by WGS reaction. The major products are highlighted in Fig. 12. Corma et al. [48] proposed a more complex reaction mechanism which was highly similar to the reaction pathways of Tsukuda et al. [192] and Chai et al. [96]. Additionally, they added the reactions for acetaldehyde formation to Tsukuda's and Chai's proposed mechanisms. Moreover, Suprun et al. [131] proposed the consecutive reaction mechanism initiated from by-products such as acetol and 3-HPA. They demonstrated the formation of formaldehyde and acetaldehyde that Tsukuda et al. [192] illustrated in his reaction pathway.

Deleplanque et al. [136] proposed a reaction mechanism of glycerol dehydration which involved the influence of oxygen co-feeding on it (Fig. 13). According to the literature, it is the first loss of water caused to hydroxyacetone and 3-hydroxypropanal production. This is followed by second dehydration of 3-hydroxypropanal leading to acrolein formation, the major product. Furthermore, formaldehyde and acetaldehyde can be produced from retroaldol reaction of 3-hydroxypropanal. In this case,

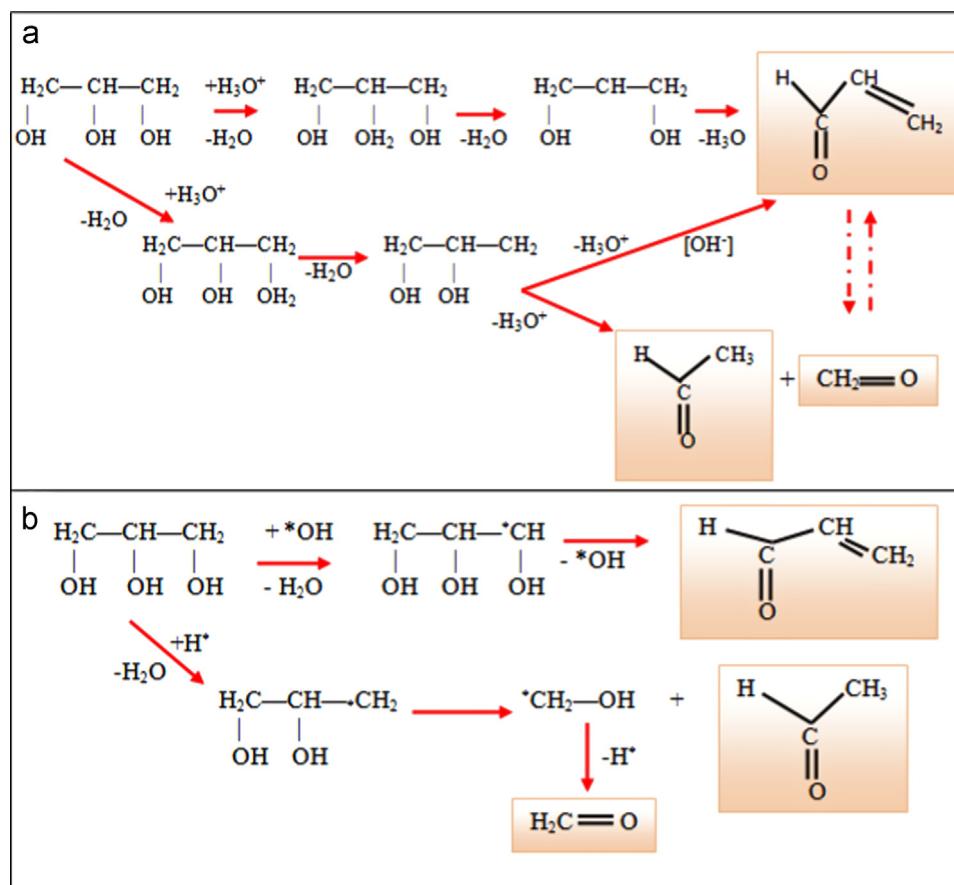


Fig. 10. Mechanism for formation of acetaldehyde, acrolein, and formaldehyde [171].

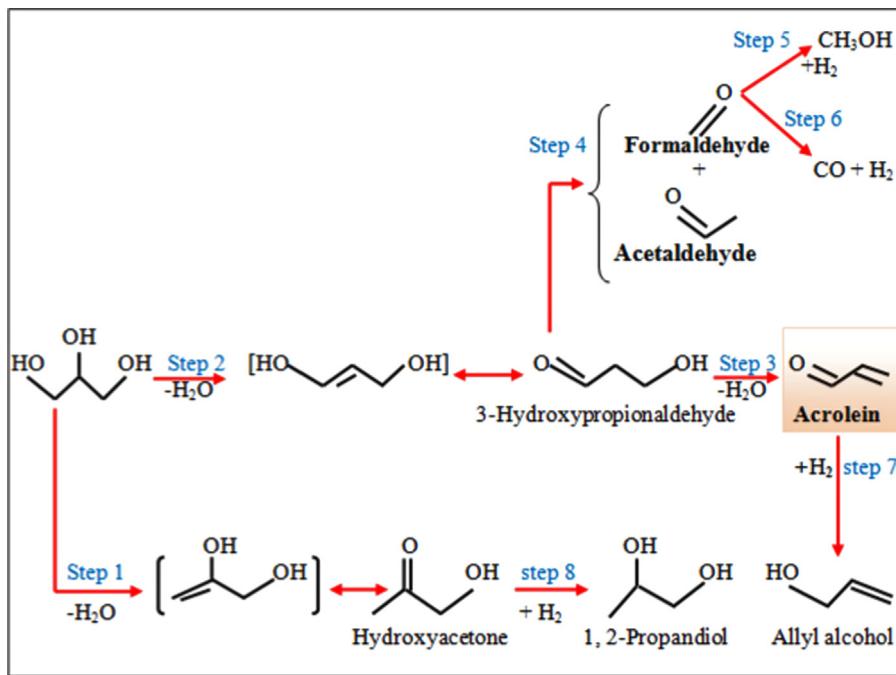


Fig. 11. Mechanism of glycerol dehydration in presence of solid acid catalyst [96].

formaldehyde can react with glycerol or oxygen to produce cyclic ether or formic acid and carbon oxides (CO_x), respectively. Coke formation on the catalyst surface changed the catalyst activity for the production of acetaldehyde, propanal, and hydroxyl-acetone. They concluded that oxygen presence improved the formation of oxidation products such as acetic acid, carbon oxides (CO_x), propenoic, and formic acid. Meanwhile, acrylic acid formation depended on the catalyst suitability. The red color in Fig. 13 illustrates the products formed by oxygen co-feeding.

Alhanash et al. [101] proposed new reaction pathways of dehydration of glycerol to acrolein over Lewis and Bronsted acids. They reported that high acrolein concentration was produced by Bronsted acid sites due to the direct protonation of the secondary glycerol hydroxyl group. However, Lewis acid sites produced acetol due to the activation of the terminal glycerol OH-group. Lewis acid sites can reform the initial Lewis acid site by water losses or can be reformed to the pseudo-Bronsted acids sites with characteristics suited for glycerol dehydration. Consequently, the Lewis acid catalyst enhances acetol selectivity (Fig. 14).

Fig. 15 illustrates the new reaction mechanism for glycerol dehydration to acrolein over solid acid catalyst. Martinuzzi et al. [160] proposed a new reaction mechanism for glycerol dehydration to acrolein (Fig. 15). According to Corma et al. [48] methylglyoxal forms 2,3-hydroxypropanal. However, in this study Martinuzzi et al. [160] could not detect 2,3-hydroxypropanal and also 1,2-propanediol. Therefore, they decided to assume these are two intermediate products in this research. Besides, acetol formation could not be the only reason for a huge amount of methylglyoxal production in this research. Due to the absence of allylic alcohol in this experiment, researchers concluded that it formed directly from glycerol. According to Deleplanque et al. [136], the appearance of 1,3-dioxa-5-ol was a consequence of cyclizing glycerol and formaldehyde. New pathways for dehydrogenation of allylic alcohol to acrolein were detected. Also, propanal created during different reaction pathways of isomerization of allylic alcohol and 1,2-propanediol dehydration while acetaldehyde forms by propanal C-C bond cleavage. The other new aspects of this mechanism were phenol produced only from acetone, methanol

from formaldehyde, ethanol by hydrogenation of acetaldehyde, 2,3-butanediol from methylglyoxal, methacrolein from acrolein, and finally aldol condensation of acetaldehyde and acetone had caused cyclopenten formation.

Kongpatpanich et al. [206] investigated both the reaction mechanism and structure studies of glycerol dehydration to acrolein and acetol over HZSM-5 catalyst by density functional theory (DFT). According to the experimental results by Corma et al. [47] the glycerol dehydration mechanism started with two different glycerol adsorption processes that include the primary OH group and secondary OH group adsorption that led to acetol and direct acrolein formation, respectively. Researchers concluded that acrolein formation was kinetically favoured compared to acetol formation. Acrolein remained as the main product of glycerol dehydration. Its reaction was less reactive in comparison to acetol. Acrolein could not convert to other products at moderate temperature. Moreover, glycerol dehydration to acrolein and acetol are both endothermic. Consequently, this increased the reaction temperature which caused to surge the forward reaction rate.

Based on the proposed reaction pathways of glycerol dehydration to acrolein some researchers have attempted to obtain the reaction energies for various reactions [170–171]. Kongpatpanich et al. [207] calculated the energies for the reaction mechanism that was proposed by Yoda et al. [208]. They used Gaussian 03 with M06-2X/6-31G set for the zeolite 12T cluster model. The results indicated that the first dehydration step required 41.4 kcal/mol energy which was higher than 22.4 kcal/mol reported by Nimlos et al. [209]. The second dehydration step and final energy state were 38.5 and 19.5 kcal/mol. Fig. 16 shows estimated energies for glycerol dehydration in the presence of MFI-zeolite.

3.6. Application of crude glycerol for acrolein production

Application of crude glycerol instead of industrial refined glycerol is the key component for decreasing the capital and production costs of acrolein as well as other value added chemicals. Indeed, crude glycerol utilization emerges as the competitive in the industrial market versus petrochemicals industries [210].

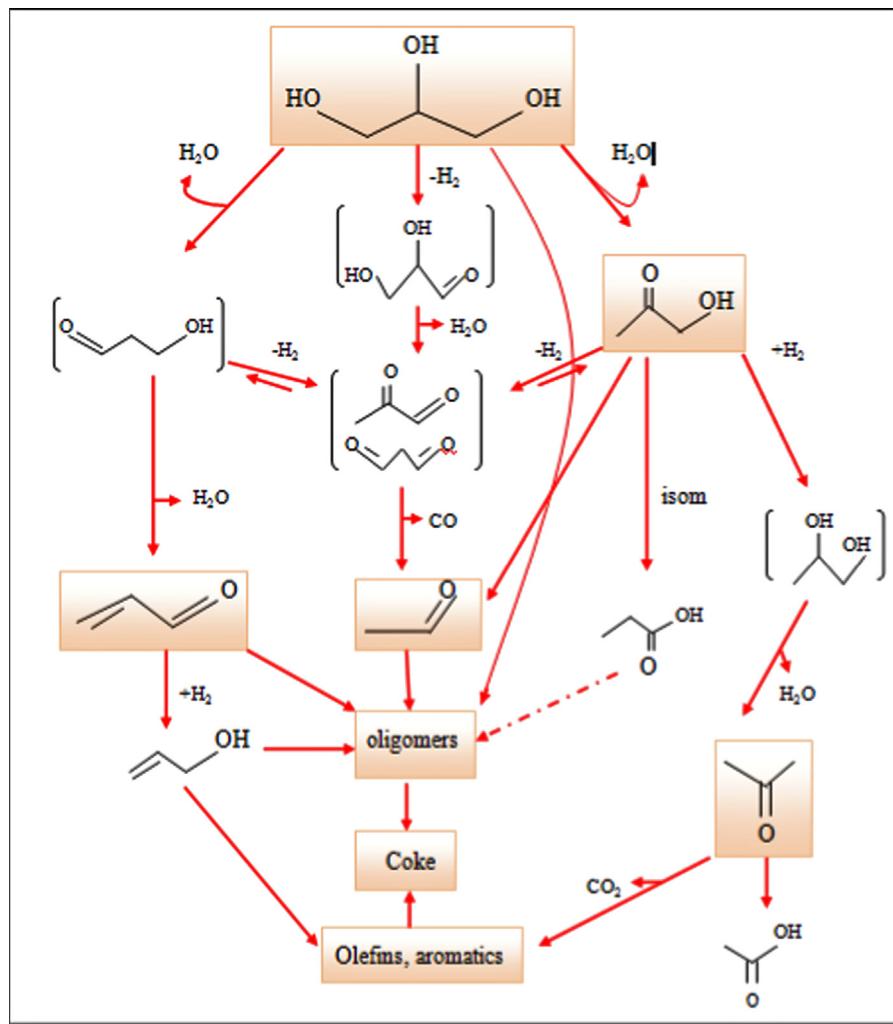


Fig. 12. Glycerol dehydration mechanism (reactant and main products have been highlighted) [48].

Besides, the price of refined and crude glycerol reduces daily depending on its progress in biodiesel industries. For instance, the refined and crude glycerol price ranges were 0.5–1.5\$/lb and 0.040–0.33\$/lb during the last few years. Table 14 lists the various prices of glycerol from 2001 to 2012 [211].

In Brazil, Leoneti et al. [212] reported a dramatic fall in the average glycerol price from 1.44 \$/kg to nearly 0.77 \$/kg in 2005 and 2012. More importantly, in some of the regions with biodiesel plants, the glycerol price is in the range of 0.29–0.34 \$/kg. However, the crude glycerol contains impurities which cause some technical problems such as the poisoning of the catalyst or plugs; this is due to the deposition of high boiling organic materials or inorganic salts.

In fact, there are only a few research activities related to the application of crude glycerol as a feedstock for the production of value added chemicals. Kijenski et al. [213] used evaporated crude glycerol as a feed to the reactor. In this method, crude glycerol impurities remained in the liquid phase and did not transfer to the reaction process. They used a mixture of 75 wt% glycerol and 3 wt % impurity which was then added to silicon-oil heated at 603 K. Furthermore, Dubois [214] and Sereshiki et al. [215] proposed a fluid inert solid be heated to high temperature. This process, with continuous regeneration, caused glycerol to evaporate; whereas the impurities remained in the fluidized bed. They reported application of a solution of 18 wt% glycerol and 2 wt% sodium chloride in contact with a silica particle fluidized bed at 583 K. The results indicated 99.9% separation and recovery of the initial sodium chloride in the final product.

Dubois [216] patented another process with crude glycerol application for acrolein production. He claimed that acetals could be formed in the first reaction step from glycerol to acrolein. Indeed, lower boiling point (453–513 K) of acetals decreased undesired reactions compared to glycerol (563 K). Finally, acrolein was formed after two steps: evaporation and dehydration of acetals over acid catalysts. Fig. 17 illustrates the reaction mechanism of this process.

These methods which aim to decrease crude glycerol impurities all related to glycerol being produced by conventional (homogeneous catalyst) biodiesel production process. Hence, the application of a new generation of heterogeneous catalyst revealed that final crude glycerol has more than 98% purity [24]. In fact, this process totally eliminates the downstream needs for crude glycerol separation and purification. However, compared to conventional processes, these new industrial processes also have their own drawbacks. For example, capital and production costs are higher. Therefore, this topic still requires more research and study to find the best solution.

4. Techno-economical evaluation of bio-based acrolein production

Several groups have evaluated the economics of the bio-based acrolein and acrylic acid productions from glycerol. For instance, Corma et al. [48] reported 58% carbon acrolein yield by 85 wt% glycerol conversion. They provided a comprehensive cost

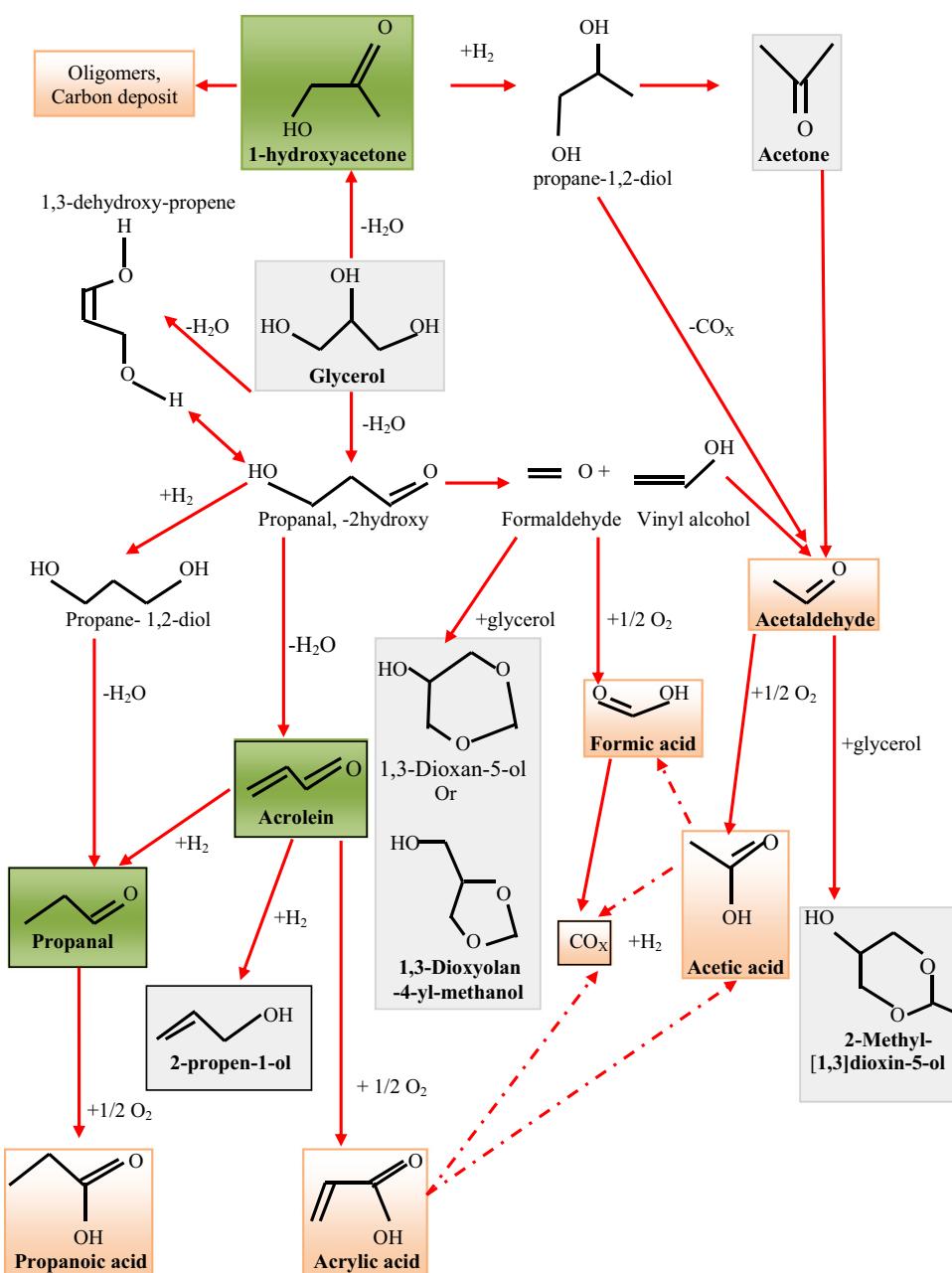


Fig. 13. Dehydration of glycerol in presence of oxygen [136]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

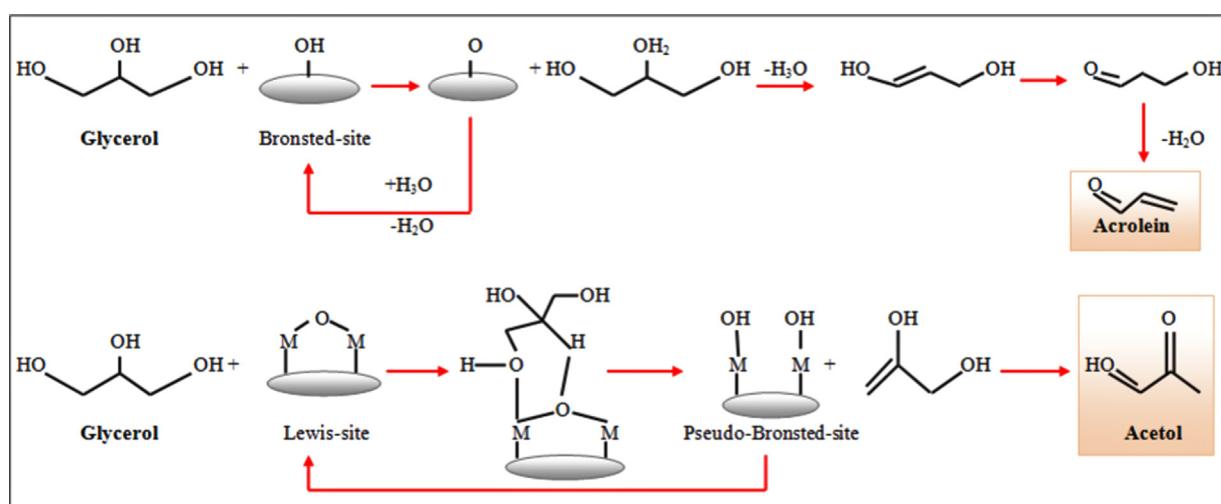


Fig. 14. Reaction mechanisms over (a) Brønsted acid and (b) Lewis acid catalysts [101].

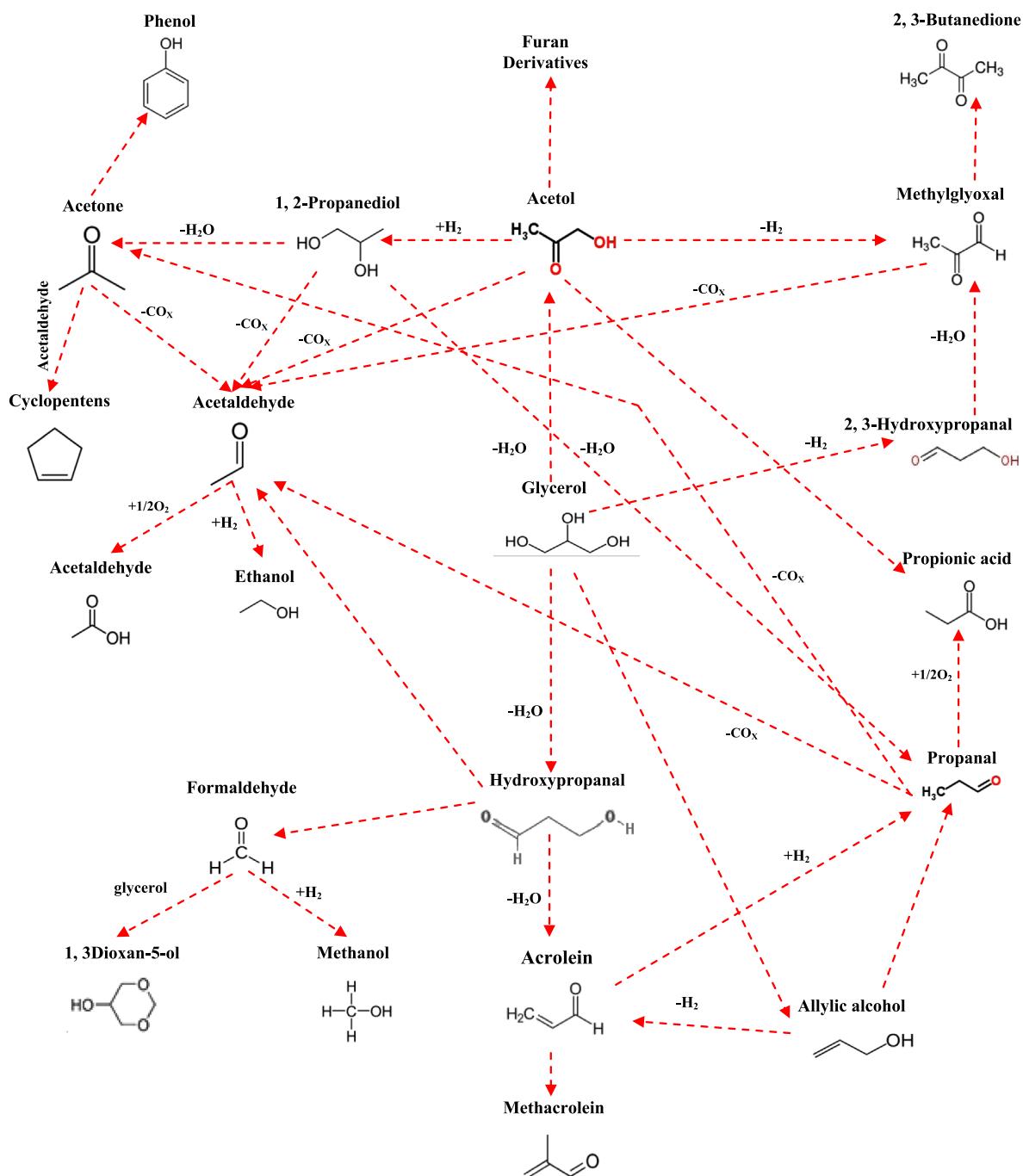


Fig. 15. New proposed reaction mechanism for glycerol dehydration to acrolein over solid acid catalyst [160].

evaluation for acrolein production. By considering 1000 \$/ton feedstock costs for propene and 300 \$/ton for glycerol solution, the production cost for the glycerol- and propene-based processes were 1120 and 900 \$/ton of acrolein, respectively. The acrolein production from crude glycerin was competitive with acrolein produced by propylene oxidation. They also claimed that the price of acrolein produced from glycerol can be improved by enhancing the yields of acrolein (28% in this research) in the process that theoretically is 52 wt% from the raw glycerol solution.

Ott et al. [172] performed raw material cost evaluation. The glycerol and acrolein prices were 150 € t^{-1} and 342 € t^{-1} , respectively. The calculations were based on the usage of 60% crude glycerol as feedstock and 75 mol% acrolein yield. They also claimed that by reasonable energy management, and optimum acrolein

yield and also increasing crude oil price, it is possible for the acrolein process via catalytic dehydration of glycerol to economically and ecologically compete with the crude oil based process.

Posada et al. [217] proposed different simulations and economical evaluations for utilization of glycerol as a raw material for production of 9 value-added chemicals (syngas, acrolein, 1,2-propanediol, ethanol, 1,3-propanediol, D-lactic acid, succinic acid, propionic acid, and poly-3-hydroxybutyrate). The results indicated that 85.2% acrolein yield at 100% glycerol conversion obtained in the proposed model. Fig. 18a illustrates the schematic diagram of the proposed simulated model. The economical evaluations of this process demonstrated that the ratio of commercial scale price and the total production costs for 92 wt% and 98.5% acrolein purity were 1.34 and 0.99, respectively. In addition, the main contribution

of the production costs of 92 wt% and 98.5 wt% purity of acrolein are raw material and utilities by 72.45% and 83.22%. Indeed, for high purity (98.5 wt%) acrolein total production costs were equal to the total sale price and there was no profit in this process. However, lower purity (92 wt%) acrolein showed 35% profitability, due to the ratio of 1.34. Fig. 18b shows the ratio of commercial scale price and production costs and Fig. 18c illustrates share of the acrolein production costs.

The worldwide ratio of sale price and total production costs for all nine value-added chemicals produced from glycerol in the study is depicted in Fig. 18d. All the value-added chemicals were

economically viable due to the ratio larger than one. In fact, 1,3-propanediol and 1,2-propanediol were the most profitable products with the ratio 1.83 and 1.57, respectively. However, hydrogen and succinic acid production were not highly economical, due to the lowest amount of profits 5% and 8%, respectively. Surprisingly, this figure revealed that glycerol purification was more profitable than acrolein and ethanol production. However, this situation will change in the future with technological advancement, higher selectivity and conversion in acrolein production process.

In addition, Liu et al. [62] for the first time compared the bio-based (glycerol dehydration) and petroleum-based (partial oxidation of propylene) acrolein production processes by the simulation method. They evaluated both propylene- and glycerol-based processes for annual production of 10000 t of acrolein. This amount was based on the annual production of glycerol from biodiesel plants and also other approaches of value-added chemicals production from glycerol such as lactic acid [218], 1,3-propanediol [219], and epichlorohydrin [220].

Table 15 compares the major components in the two production processes. Clearly, there are many similarities between the two processes, and multiple PBR system seems to be well applicable to both production methods. There are some important factors to be considered. The propylene oxidation is highly exothermic, while the glycerol dehydration is endothermic. Thus, a heat exchanger is required for the multiple PBRs in the propylene-based production method to release the heat, while in bio-based production methods for multiple PBRs, a furnace is needed to maintain the reaction at high temperature. Moreover, the operating pressure of the PBR for propylene-based production is usually in the range of 150–250 kPa, which is usually higher than that of bio-based acrolein production

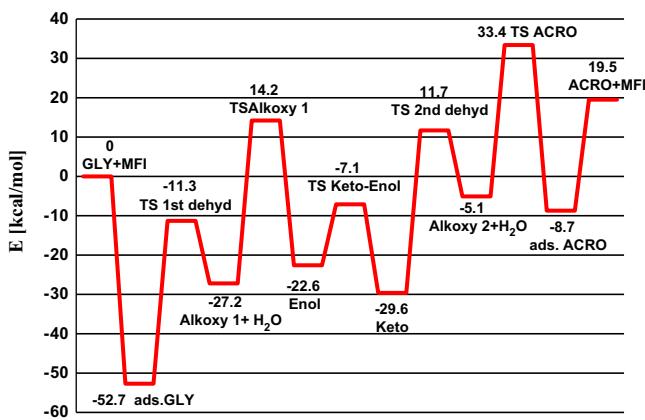


Fig. 16. Estimated energies for glycerol dehydration in presence of MFI-zeolite [209].

Table 14

Annual price of glycerol from 2001 to 2012 [211].

Type of glycerol	Glycerol price (cent per pound)											
	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Synthetic	72	73	90	85	85	—	—	—	—	—	—	—
Refined	60	58	65	55	45	35	70.5	55	41	38	37	34
Crude	15	12	12	10	5	2	10	5	6	7	2	4

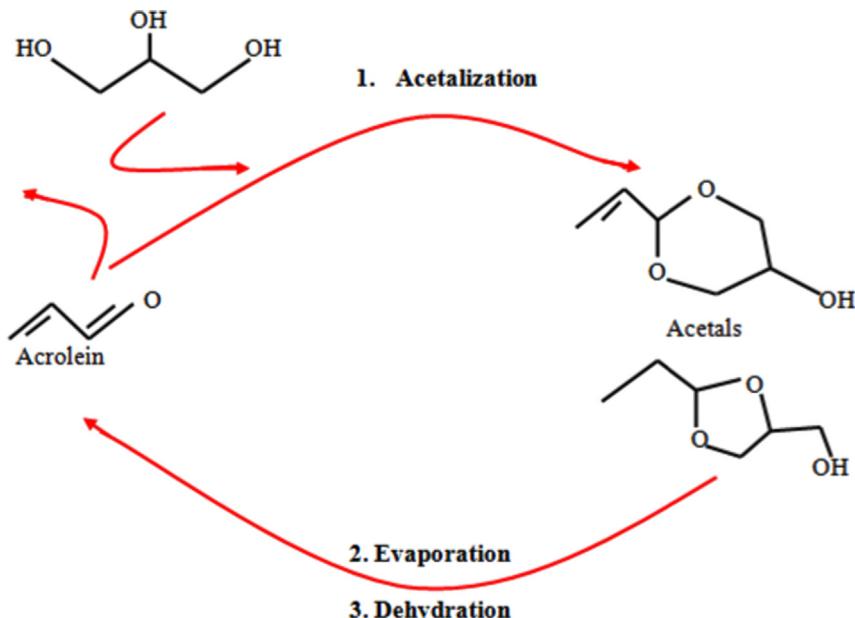


Fig. 17. Crude glycerol purification based on intermediate acetalization [10].

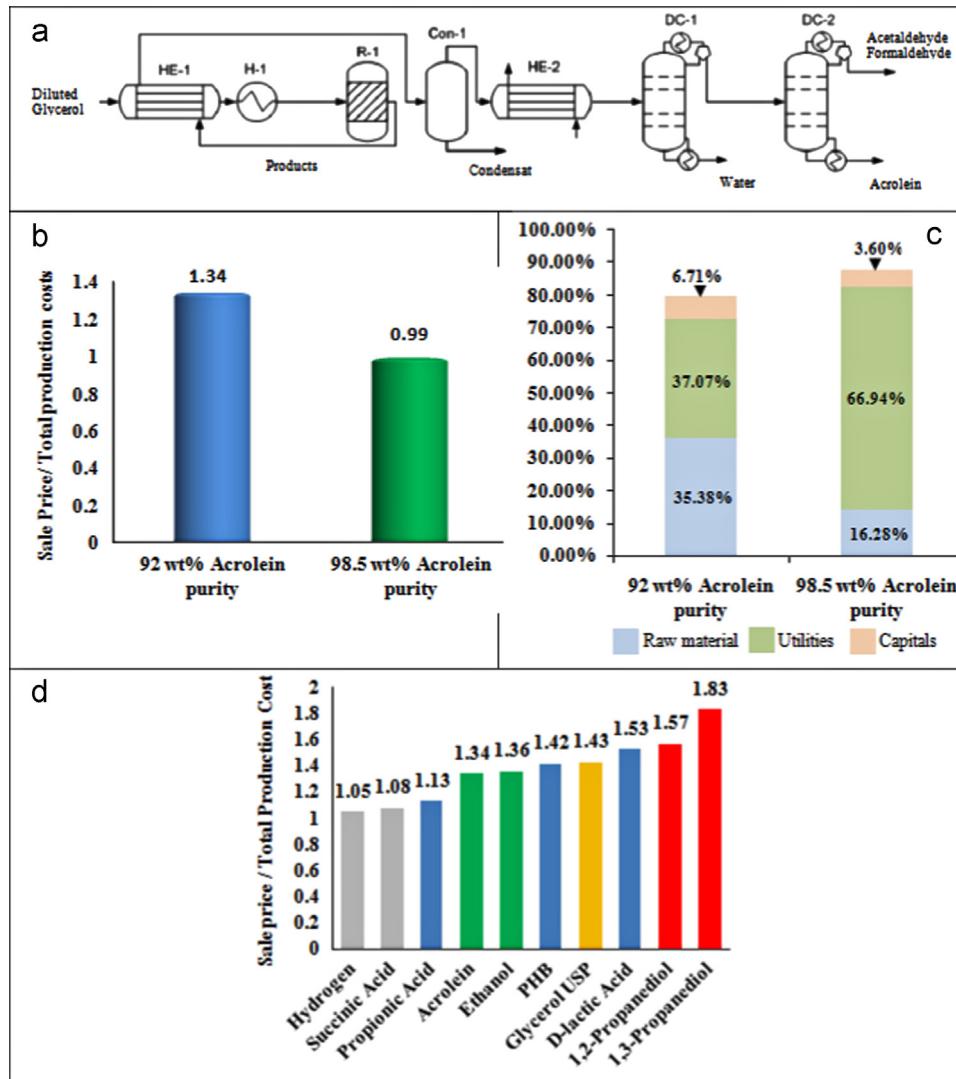


Fig. 18. Simulation and economical evaluation related to industrial production of acrolein and other value added chemicals from glycerol [217].

operated at atmospheric pressure. As a result, the fixed costs for the reactor part would not differ much for both processes.

Furthermore, there are some differences that are related to the cost of energy, feedstock, labor, and catalyst. An additional nitrogen generator for acrolein production is needed in bio-based process that costs 23,340\$. Also, in this process a mixing/agitation tank is required to mix hot glycerol with steam. In variable costs, there are several major components that vary between the bio-based and propylene-based methods for a 10,000t/year acrolein production that are listed in Table 16.

The amount of feed stocks for bio-based and propylene-based methods is calculated based on a stoichiometric relation assuming 80 mol% acrolein yield while the amount of crude glycerol calculated is based on 80 % glycerol purity. According to Table 16, the total cost of bio-based dehydration of refined glycerol is 12.95–16.13 million (MM) \$, which is 0.82–1.02 times less than propylene-based approach. Moreover, application of crude glycerol for the bio-based method required 2.71–5.83 MM\$ costs, that is 17.2–40.5% of the propylene-based process costs. The feedstock cost is the most important element in the variable costs.

Liu et al [62] also reported an indirect method to evaluate the industrial catalyst costs. They selected active bismuth molybdate (multi-component metal) catalysts for petroleum based and silicotungstic acid catalyst for bio-based acrolein production. To

produce 10,000 t of acrolein via the propylene and glycerol based methods, 9657 and 7083 kg catalysts are needed, respectively. Thus, the highest total costs for required catalysts were 4.83 and 4.9 MM\$/year in petroleum based and bio-based processes. As a result, the acrolein production with refined glycerol approximately had similar costs with the conventional manufacturing method. However, application of crude glycerol as feedstock can decrease the costs significantly by 31–42%.

It is important to mention that the majority government policies cases and regulations are helping bio-based production. In USA, 18 billion \$ of tax incentives were approved under the Renewable Energy and Job Creation Act (H.R. 6049) in 2008 to boost carbon capture, renewable energy and energy efficiency and conservation. According to calculations by Liu et al. [62] the tax expenses for both processes are almost the same. But, in some cases the expenses for bio-based process was lower due to varieties of tax credits lowering the acrolein production cost.

With increasing governmental supports from production of biodiesel, glycerin is available widely. It is expected that the glycerin will displace about 10% of the propylene used to make acrylic acid in the next 10 years. If acrylic acid production from glycerin increases to large volumes, separate storage and handling operations will be avoided to make glycerin-based acrylic acid cost prohibitive.

Table 15

Comparative lists of reactor and separation columns for the propylene-based and bio-based acrolein production [62].

Petroleum-based process		Bio-based process
Pre-treatment	Heating propylene and air	Purification (if crude glycerol is used as starting material) heating glycerol, mixing glycerol with steam
PBR reactor ^a	Multiple reactors packed with multi-components metal operating at 593 K, strong exothermic reaction operating at 150–250 kPa; requires careful temperature control (good cooling system)	Multiple reactors packed with alumina-supported heteropoly acid operating at 553 K, endothermic reaction operating at atmospheric pressure, good heat isolation, needs heating supply
1st column	Quenching of the products; removing the high-boiling compounds, mainly acrylic acid and acetic acid	Quenching of the products removing the high-boiling compounds, including acetol, acetic acid, acrylic acid, phenol, and glycerol
2nd column	Feed: propylene, CO _x , steam, acrolein, acetaldehyde, propionaldehyde obtaining a diluted acrolein solution devoid of non-condensable gases	Feed: acrolein, acetaldehyde, propionaldehyde, steam, CO _x , N ₂ obtaining a diluted acrolein solution devoid of non-condensable gases
3rd column	Feed: acrolein, water, acetaldehyde, propionaldehyde. distilled: crude acrolein	Feed: acrolein, water, acetaldehyde, propionaldehyde distillate: crude acrolein
4th column	Feed: acrolein, acetaldehyde, propionaldehyde. distillate: acrolein containing less impurity	Feed: acrolein, acetaldehyde, propionaldehyde. distillate: acrolein containing less impurity
5th column	Obtaining refined acrolein; adding stabilizer	Obtaining refined acrolein; adding stabilizer

^a Packed bed reactor.

Table 16

Comparison of propylene-based and bio-based acrolein production (10,000 ton/year) regarding feedstock and energy consumption [62].

Feedstock	Price (\$/ton)	Propylene process (ton/year)	Bio-based process (ton/year)	
			Refined glycerol	Crude glycerol
Propylene	1664 ^a	9375 ^b	–	–
Refined glycerol	595.25–749.57 ^c	–	20,536 ^(d)	–
Crude glycerol	77.16–198.42 ^c	–	–	25,669 ^e
Steam	7.31	20089 ^f	82142 ^g	82,142 ^g
Energy	0.05 ^h	0	2,670,000 ^{h,i}	2670000 kWh ^{h,i}
		15.74 ^j	Total price (MMS) 12.95–16.13 ^k	2.71–5.83 ^l

^a Price reported in February 2011 by ICIS, [221].

^b Calculated based on 10,000 t annual acrolein production and 80 mol% acrolein yield: [10,000 t/(56 g/mol) × (42 g/mol)]/80% = 9375 t.

^c Price reported in September 2010 by ICIS, [222] apart from the lower end of crude-glycerol price [223].

^d Calculated based on 10,000 t annual acrolein production, 80 mol% acrolein yield, and stoichiometric of glycerol dehydration to acrolein: [10,000 t/(56 g/mol) × (92 g/mol)]/80% = 20,536 t.

^e Calculated based on the same assumptions as [d] and the assumption that crude glycerol contains 80% glycerol: [10,000 t/(56 g/mol) × (92 g/mol)]/80% = 25,669 t.

^f Calculated based on molar ratio of the feed propylene/air/steam = 1:10:5 and calculated propylene amount required: 9375 t/(42 g/mol) × (18 g/mol) × 5 = 20,089 t.

^g Calculated based on calculated amount of glycerol required and the assumption that the feed has a concentration of 20 wt% glycerol: 20,536 t/20% = 82,142 t.

^h \$ per kWh.

ⁱ Calculated for a year based on heat (43 kJ/mol) required for the endothermic dehydration reaction [62] and annual working hours of 8000 h: [105 t⁻¹(106 g/t)/(56 g/mol)]/80% × (43 kJ/mol) × (0.000278 kWh/kJ) = 2.67 × 106 kWh.

^j (1664 \$ t⁻¹) × (9375 t) + (7.31 \$/t) × (20,089 t) = 15.74 × 106\$ = 15.74 M\$.

^k Low: (595.25 \$/t) × (20,536 t) + (7.31 \$/t) × (82,142 t) + (0.05 \$/kWh) × (2.67 × 106 kWh) = 12.95 MM\$. High: (749.57 \$/t) × (20,536 t) + (7.31 \$/t) × (82,142 t) + (0.05 \$/kWh) × (2.67 × 106 kWh) = 16.13 MM\$.

^l Low: (77.16 \$/t) × (25,669 t) + (7.31 \$/t) × (82,142 t) + (0.05 \$/kWh) × (2.67 × 106 kWh) = 2.71 MM\$ and High: (198.42 \$/t) × (25,669 t) + (7.31 \$/t) × (82,142 t) + (0.05 \$/kWh) × (2.67 × 106 kWh) = 5.83 MM\$.

There are some industrial plants that are currently using glycerol as a feedstock for acrolein and acrylic acid production. In 2004, Arkema developed a method to produce acrylic acid from renewable resources. Large glycerin by-product remained from castor oil to produce nylon. In the classic method to produce acrylic acid, propylene is converted into acrolein before acrylic acid is produced in a following process. The researchers decided to replace propylene with glycerin. Compared to propylene, glycerin is a viscous and polar liquid, and all water that is attached to the glycerin should be separated out before producing acrolein.

In 2009, Arkema and HTE, a German company, developed a series of catalysts to produce acrolein from glycerin. They developed catalysts that enabled Arkema to convert glycerin directly into acrylic acid without producing acrolein using 14 \$ million grant over a 3-years funded research.

Some other companies like Nippon Shokubai, in Japan, have also tried to develop catalysts that convert glycerin into acrylic acid with one step. Some other companies, like Waltham, and Novomer are working on a more environmental friendly process to

produce acrylic acid with combined ethylene oxide, carbon monoxide, and catalysts. Moreover, OPX Biotechnologies Company has claimed that it has produced a cost-effective microorganism, fermenting a sugar-based feedstock into acrylic acid.

5. Conclusion and future outlooks

The review paper has provided information about (1) spectacular opportunities for production of value-added chemicals from glycerol, particularly acrolein as one the most important intermediates in industry, (2) wide application of glycerol as feedstock for refineries with impact to reduce the economical drawbacks of biodiesel production, and (3) reduction of environmental concerns by application of bio-renewable feedstock as a substitute of fossil fuels particularly crude oil.

As a result of various environmental concerns (global warming, CO₂ emission, fossil fuel resources depletion), steep hike of fossil fuels price, and increasing fossil fuels demands a large number of

researchers have proposed biofuels (bio-ethanol and biodiesel) as the substitute for non-renewable fuels. Consequently, huge amount of crude glycerol have been available in the market recently, but unfortunately it is burnt in some cases as a waste material.

The unique characteristics of glycerol make it a highly demanding material for researchers to produce marketable chemicals by catalytic conversion of renewable sources. This review presents many possible methods for catalytic dehydration of glycerol to acrolein. Acrolein has wide application for various products such as superabsorbent polymers, DL-methionite, and acrylic acid which have significant uses in the chemical and food industries.

Homogeneous catalyst leads to pollution, equipment corrosion, and increasing production costs. The introduction of new heterogeneous catalysts has attracted a great deal of researchers' attention in this area. In addition, the strength of acidity and textural properties of catalyst have noticeable influence on catalytic performance. Glycerol dehydration to acrolein can occur in both gas- and liquid-phases.

The application of three main groups of catalysts (HPAs, zeolites, and metal oxides) for glycerol dehydration to acrolein in gas phase reviewed in this study. The Cs/HPW catalyst displayed the best ever reported acrolein yield of 98%. However, the catalyst activity lasted for only a few hours. Besides, the 50%HPW/Cs-SBA catalyst exhibited remarkable results with 86% acrolein selectivity at complete glycerol conversion, and 170 h of stability, which was the best among HPA supported catalysts. Meanwhile, the best result reported for zeolite group was 92.6% acrolein selectivity at complete glycerol conversion over SBA-SO₃H catalyst. This catalyst achieved 80% acrolein selectivity even after 140 h which was one of the most stable catalysts in this group. Finally, according to the reviewed literatures in this study the highest ever reported acrolein yield for metal oxides catalysts (Fe_x(PO₄)_y) was 92.6% at 100% glycerol conversion and 25 h stability. This group of catalysts has many parameters for evaluation and investigation such as different synthesis methods and their binary or tertiary combination effects on the catalyst activity. Recently, application of different ionic liquid catalysts for dehydration of glycerol to acrolein was reported. The yield could reach up to 57.4% in liquid phase. Research on this group of catalysts will be expanded in future due to their environmental friendly characteristics.

The main obstacle for industrial application of glycerol dehydration to acrolein seems to be fast catalyst deactivation as a result of carbon deposition (coke) on the catalyst surface. Various approaches such as co-feeding of oxygen, hydrogen, and sulfur dioxide are applied to slowdown the catalyst deactivation. Oxygen co-feeding, however, is reported to be the most convenient approach compared to fluidized and pulse-wise regeneration processes due to lower costs and easier operation.

Existing literatures on liquid phase dehydration of glycerol to acrolein has also been studied in this review. It seems that the supercritical water conditions and effect of acidic catalysts in supercritical condition led to some problems such as high stress on reactor.

Another hurdle that limits the utilization of glycerol as a raw material is its high cost. If the glycerol price decreases, some new products (e.g. polymer) can be produced economically. In addition, crude glycerol, produced by biodiesel plants, is the cheapest feedstock that can be used as a substitute for pure glycerol. A few studies simulated the economical evaluation of the bio-based acrolein production process. As a result, the commercial scale price over total production costs ratio of 1.34 proves the economical feasibility of process.

It is worthy to note that glycerol obtained as a by-product in biodiesel processes includes various impurities and cannot be used directly as a feedstock in other processes. The highest quality (98%) of crude glycerol produced by a biodiesel plant gives new hopes

for many researchers to focus on this raw material for production of acrolein. Finally, a new and stable heterogeneous catalyst that can be regenerated and recycled for crude glycerol conversion at the commercial and industrial levels for catalytic dehydration of glycerol to acrolein is highly sought after.

The main recommendations that we can propose here are

- There are many researches for glycerol dehydration to acrolein in gas- and liquid-phases using different catalysts (HPAs, zeolites, and mixed metal oxides), but still there is no catalyst which exhibits long-term stability without severe deactivation with prospect for industrial application.
- Crude glycerol application opens new perspective on waste minimization and cost reduction in industry. However, the limited number of studies for utilization of crude glycerol for value-added chemicals production is the main drawback for rapid industrialization of this process.
- Liquid phase catalytic dehydration of glycerol to acrolein showed encouraging results recently. Thus, it requires more attention in this field, particularly application of modified heterogeneous catalysts (HPA, zeolite, mixed metal oxides) to the dehydration process.
- Limited numbers of studies related to application of ionic liquid catalysts have been reported. New research will be expanded in near future due to the environmental friendly characteristics of ionic liquids.
- The kinetic parameters of the majority of reactions in acrolein production by glycerol dehydration over various catalysts should be determined to provide better understanding of reaction optimal conditions and for reactor design purposes.
- Simulation and modeling of glycerol dehydration to acrolein in different reaction conditions and processes by various methods such as ASPEN can enhance our knowledge for possible commercialization and industrialization of this process.
- Majority of researchers have only focused on application of batch and fixed-bed reactors. Application of other types of reactors and processes such as membrane reactors, ultrasonic, and microwave should significantly improve the reaction conditions (reaction time and reaction temperature) and acrolein yield.

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